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# UTILITY PATENT APPLICATION SUBMITTAL

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## APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

1. ☒ Specification [Total Pages 73]
2. ☒ Drawing(s) (35USC 113) [Total Pages 17]
3. ☒ Declaration and Power of Attorney [Total Pages 2]
- a. ☐ Newly executed declaration (Original copy)
- b. ☐ Copy from prior application (37CFR 1.63(d))  
(for continuation/divisional with Box 14 completed)
- i. ☐ [Note Box 4 Below]  
**DELETION OF INVENTOR(S)**  
Signed statement attached deleting  
inventor(s) named in the prior application,  
see 37 CFR 1.63(d)(2) and 1.33(b)
4. ☐ Incorporation By Reference (usable if Box 3b is checked)  
The entire disclosure of the prior application, from which a  
copy of the oath or declaration is supplied under Box 3b,  
is considered as being part of the disclosure of the  
accompanying application and is hereby incorporated by  
reference therein.

## ACCOMPANYING APPLICATION PARTS

5. ☐ Assignment Papers (cover sheet & documentation)
6. ☒ Letter under 37 CFR 1.41(c).
7. ☐ English Translation Document (if applicable)
8. ☐ Information Disclosure Statement (IDS)/PTO-1449
9. ☒ Preliminary Amendment
10. ☒ Return Receipt Postcard (MPEP 503)  
(Should be specifically itemized)
11. ☐ Small Entity Statement filed in prior application,  
Statement(s) Status still proper and desired
12. ☒ Certified Copy of Priority Document(s) Japanese  
Application Nos P11-146653 filed May 24, 1999 and P11-  
365064 filed Dec. 22, 1999
13. ☐ Other:

14. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) ☐ of prior application No: /

### CLAIMS AS FILED

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☒ The Commissioner is hereby authorized to charge any additional fees which may be required in connection with this application, or credit any overpayment to ACCOUNT NO. 08-2290. A duplicate copy of this sheet is enclosed.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

**PRELIMINARY AMENDMENT ACCOMPANYING APPLICATION**

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ATTORNEY DOCKET NO P00,0483

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INVENTION: **SOLID ELECTROLYTE BATTERY**

Assistant Commissioner of Patents and Trademarks  
Washington DC 20231

S I R:

Between the title and the heading "Background of the Invention" on page 1, insert the following:

—RELATED APPLICATION DATA

The present application claims priority to Japanese Application No. P11-146653 filed May 26, 1999 and Japanese Application No. P11-365064 filed December 22, 1999, which applications are incorporated herein by reference to the extent permitted by law.--

Respectfully submitted,

  
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TITLE OF THE INVENTION

SOLID ELECTROLYTE BATTERY

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a solid electrolyte battery incorporating a solid electrolyte, and more particularly to a solid electrolyte battery incorporating a separator which has specific mechanical strength and thermal characteristics so as to considerably improve its energy density and safety.

Description of the Related Art

As a power source for a portable electronic apparatus, such as a portable telephone or a notebook personal computer, battery is an important element. To reduce the size and weight of the electronic apparatus, enlargement of the capacity of the battery and reduction in the volume of the same have been required. From the foregoing viewpoints, a lithium battery exhibiting a high energy density and output density is suitable to serve as the power source of the portable electronic apparatus. The lithium battery incorporating a negative electrode constituted by a carbon material has a mean discharge voltage of 3.7 V or higher. Moreover, deterioration caused from charge and discharge cycles can relatively satisfactorily be prevented. Therefore, the lithium battery has an advantage that a high energy density can easily be realized.

The lithium batteries are required to permit a variety of shapes to be formed

which include a battery having flexibility and a high degree of freedom of the shape, a sheet battery having a small thickness and a large area and a card battery having a small thickness and a small area. A conventional structure that battery elements, which are a positive electrode and a negative electrode, and electrolytic solution are enclosed in a metal can encounters a difficulty in forming the various shapes. Since the electrolytic solution is employed, the manufacturing process becomes too complicated. Moreover, a countermeasure against leakage of the solution must be taken.

To solve the above-mentioned problems, batteries have been researched and developed which include batteries each of which incorporates a solid electrolyte composed of a conductive and organic polymer or inorganic ceramics and a gel-like solid electrolyte (hereinafter called a "gel electrolyte") in which matrix polymers are impregnated with electrolytic solution. The solid electrolyte battery incorporating the solid electrolyte and the gel electrolyte battery include the fixed electrolytes. Therefore, contact between the electrode and the electrolyte can be maintained. Hence it follows that the foregoing batteries are free from a necessity for enclosing the electrolytic solution by employing a metal can or exerting pressure on the battery element. A film-shape case material can be used to reduce the thickness of the battery. Thus, an energy density higher than that of a conventional battery can be realized.

In general, the solid electrolyte of the solid electrolyte battery has proper mechanical strength as disclosed in "MATERIAL TECHNIQUE OF

HIGH-PERFORMANCE SECONDARY BATTERY AND EVALUATION, APPLICATION AND DEVELOPMENT OF THE SAME" (Technical Information Association, 1998). Therefore, a structure of the battery distinct from that of the conventional battery incorporating the electrolytic solution can be selected. For example, a fact has been reported that any separator is not required between the positive electrode and the negative electrode. The foregoing fact has been known as an advantage of the solid electrolyte.

The reported solid electrolyte suffers from unsatisfactory strength including piercing resistance as compared with the conventional separator constituted by a polyolefine small-pore film and the like. When the thickness of the solid electrolyte of the conventional solid electrolyte battery is reduced to, for example, 40  $\mu\text{m}$  or smaller to raise the energy density, there arises a problem in that internal short circuit frequently occurs after the battery has been manufactured by performing an assembling process. As described above, the energy density of the solid electrolyte battery cannot easily be raised by reducing the thickness of the solid electrolyte layer.

As for heat resistance which is an index to evaluate the reliability of the battery, the conventional solid electrolyte battery suffers from unsatisfactory heat resistance. A portion of marketed batteries is arranged to use a so-called "shutdown effect" to improve the heat resistance. On the other hand, any solid electrolyte material for the solid electrolyte battery having the shutdown effect has not been found.

As for the reliability and safety of the battery, the reliability and safety cannot

easily be realized as the energy density of the battery is raised. Therefore, also a technique for maintaining the safety of the solid electrolyte battery must be considered when a solid electrolyte battery is designed to raise the energy density.

A thin battery incorporates a separator which is made of polyolefine. In particular, a polyethylene separator is employed.

In a usual state, when the temperature of the battery has melted down and, therefore, short circuit occurs between the positive electrode and the negative electrode, thermorunaway does not occur. In a case where a battery is used in an abnormal environment, for example, in a case where the temperature of a battery charged to a voltage level higher than a usual level has been raised, there is apprehension that an accident occurs. In the foregoing case, there is apprehension that use of a separator made of polyethylene having a melt-down temperature which is lower than that of polypropylene causes melt-down of the separator to take place. That is, breakage of the separator occurs, causing short circuit between the positive electrode and the negative electrode to take place. Thus, there is apprehension that the battery generates heat.

#### SUMMARY OF THE INVENTION

In view of the foregoing, an object of the present invention is to provide a solid electrolyte battery having a high energy density and improved safety.

To achieve the object, according to one aspect of the invention, there is

provided a solid electrolyte battery including: a positive electrode; a negative electrode disposed opposite to the positive electrode; a separator disposed between the positive electrode and the negative electrode; and solid electrolytes each of which is disposed between the positive electrode and the separator and between the separator and the negative electrode, wherein the separator is constituted by a polyolefine porous film, the polyolefine porous film has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$  and a vacancy ratio satisfying a range not lower than 25 % nor higher than 60 %, and the impedance in the solid electrolyte battery is higher than the impedance realized at the room temperature when the temperature of the solid electrolyte battery satisfies a range not lower than 100°C nor higher than 160°C.

The solid electrolyte battery according to the present invention incorporates the separator constituted by the polyolefine porous film having a specified thickness, vacancy ratio and a thermal characteristic. Thus, the energy density can be raised and the safety of the same can be improved.

According to another aspect of the present invention, there is provided a solid electrolyte battery including: a positive electrode; a negative electrode disposed opposite to the positive electrode; a separator disposed between the positive electrode and the negative electrode; and solid electrolytes each of which is disposed between the positive electrode and the separator and between the separator and the negative electrode, wherein the separator is constituted by a polyolefine porous film, the polyolefine porous film has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor

larger than 15  $\mu\text{m}$ , a vacancy ratio satisfying a range not lower than 25 % nor higher than 60 %, breaking strength lower than 1650  $\text{kg}/\text{cm}^2$  and breaking ductility not lower than 135 %.

The solid electrolyte battery according to the present invention incorporates the separator constituted by the polyolefine porous film having a specified thickness, vacancy ratio and a thermal characteristic. Thus, the energy density can be raised and the safety of the same can be improved.

According to another aspect of the present invention, there is provided a solid electrolyte battery including: a positive electrode; a negative electrode disposed opposite to the positive electrode; a separator disposed between the positive electrode and the negative electrode; and solid electrolytes each of which is disposed between the positive electrode and the separator and between the separator and the negative electrode, wherein the separator is constituted by a composite material of polyethylene and polypropylene, the polyolefine porous film has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$ , the shutdown temperature is substantially the same as the shutdown temperature of a separator constituted by polyethylene and the meltdown temperature is higher than the meltdown temperature of a separator constituted by polypropylene by a range satisfying a range not lower than 10°C nor higher than 30°C.

The solid electrolyte battery according to the present invention incorporates the separator constituted by a composite material of polyethylene and polypropylene.



Thus, the energy density can be raised and the safety of the same can be improved.

According to another aspect of the present invention, there is provided a solid electrolyte battery including: a positive electrode; a negative electrode disposed opposite to the positive electrode; a separator disposed between the positive electrode and the negative electrode; and solid electrolytes each of which is disposed between the positive electrode and the separator and between the separator and the negative electrode, wherein the separator is formed by bonding a first separator constituted by polyethylene and a second separator constituted by polypropylene to each other, the separator has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$ , and the separator has a shutdown temperature which is substantially the same as the shutdown temperature of a separator constituted by polyethylene and a meltdown temperature which is substantially the same as the meltdown temperature of a separator constituted by polypropylene.

The solid electrolyte battery according to the present invention incorporates the separator formed by bonding the first separator constituted by polyethylene and a second separator constituted by polypropylene to each other. Thus, the energy density can be raised and the safety of the same can be improved.

Other objects, features and advantages of the invention will be evident from the following detailed description of the preferred embodiments described in conjunction with the attached drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view showing an example of the structure of a solid electrolyte battery according to the present invention;

Fig. 2 is a cross sectional view taken along line X-Y shown in Fig. 1;

Fig. 3 is a perspective view showing a state where a positive electrode and a negative electrode are formed into a wound electrode;

Fig. 4 is a perspective view showing an example of the structure of the positive electrode;

Fig. 5 is a perspective view showing an example of the structure of the negative electrode;

Fig. 6 is a photograph showing a fibril structure of a separator according to the present invention;

Fig. 7 is a perspective view showing an example of the structure of the solid electrolyte battery according to the present invention;

Fig. 8 is a cross sectional view taken along line X-Y shown in Fig. 7;

Fig. 9 is a perspective view showing a state where a positive electrode and a negative electrode are formed into a wound electrode;

Fig. 10 is a perspective view showing an example of the structure of the positive electrode;

Fig. 11 is a perspective view showing an example of the structure of the negative electrode;

Fig. 12 is a cross sectional view showing an example of a separator according to the present invention;

Fig. 13 is a schematic view showing the relationship between the width of the separator and that of the electrode;

Fig. 14 is a cross sectional view showing an example of the structure of a casing film;

Fig. 15 is a graph showing the relationship between the temperature of the battery according to Example 1 and the internal impedance of the same;

Fig. 16 is a graph showing the relationship between the temperature of the battery according to Example 6 and the internal impedance of the same;

Fig. 17 is a graph showing the relationship between the breaking strength and the breaking ductility of each of separators of batteries according to Examples 1 to 7; and

Fig. 18 is a photograph showing the fibril structure of the separator of the battery according to Example 6.

### Detailed Description of the Preferred Embodiments

#### First Embodiment

Embodiments of the present invention will now be described.

An example of the structure of a gel electrolyte battery 1 according to this embodiment is shown in Figs. 1 and 2. The gel electrolyte battery 1 incorporates an

elongated positive electrode 2; an elongated negative electrode 3 disposed opposite to the positive electrode 2; a gel electrolyte layer 4 formed on each of the positive electrode 2 and the negative electrode 3; and a separator 5 disposed between the positive electrode 2 having the gel electrolyte layer 4 formed thereon and the negative electrode 3 having the gel electrolyte layer 4 formed thereon.

The gel electrolyte battery 1 has a structure that the positive electrode 2 having the gel electrolyte layer 4 formed thereon and the negative electrode 3 having the gel electrolyte layer 4 formed thereon are laminated through the separator 5. Moreover, a wound electrode 6 shown in Fig. 3 is formed by winding the positive electrode 2 and the negative electrode 3 in a lengthwise direction. The wound electrode 6 is covered with a casing film 7 so as to hermetically be sealed. A positive-electrode terminal 8 is connected to the positive electrode 2, while a negative-electrode terminal 9 is connected to the negative electrode 3. The positive-electrode terminal 8 and the negative-electrode terminal 9 are sandwiched in a sealing portion which is the outer periphery of the casing film 7. Each of portions in which the positive-electrode terminal 8 and the negative-electrode terminal 9 are in contact with the casing film 7 is provided with the resin film 10.

As shown in Fig. 4, the positive electrode 2 incorporates a positive-electrode active material layer 2a containing a positive-electrode active material and formed on each of the two sides of a positive-electrode collector 2b. The positive-electrode collector 2b is constituted by, for example, metal foil, such as aluminum foil.

The positive-electrode active material may be a composite lithium oxide, such as cobalt acid lithium, nickel acid lithium or spinel manganese acid lithium. The composite lithium oxide may be employed solely or a plurality of the foregoing materials may be employed.

It is preferable that the composite lithium oxide has a mean particle size of 15  $\mu\text{m}$  or smaller. When the composite lithium oxide having the mean particle size of 15  $\mu\text{m}$  or smaller is employed as the positive-electrode active material, a gel electrolyte battery can be obtained which has low internal resistance and an excellent output characteristics.

Fig. 4 shows a state where a gel electrolyte layer 4 to be described later has been formed on the positive-electrode active material layer 2a of the positive electrode 2.

As shown in Fig. 5, the negative electrode 3 incorporate a negative-electrode active material layer 3a containing a negative-electrode active material and formed on each of two sides of a negative-electrode collector 3b. The negative-electrode collector 3b is constituted by metal foil, such as copper foil.

The negative-electrode active material may be a material to which lithium can be doped/dedoped. The material to which lithium can be doped/dedoped may be lithium, its alloy or a carbon material. Specifically, the carbon material is exemplified by carbon black, such as natural graphite, artificial graphite, pyrocarbon, cokes or acetylene black; vitreous carbon; active carbon; carbon fiber; sintered material of organic polymer; a sintered material of coffee beans; sintered material of cellulose; or

sintered material of bamboo.

The inventor has energetically performed studies. As a result, a fact has been detected that methocarbon microbead carbon graphitized at a baking temperature of about 2800°C is a preferred material. The methocarbon microbead carbon has high electro-chemical stability with respect to an electrolytic solution. Therefore, an effect can be obtained when it is combined with a gel electrolyte of a type adapted to electrolytic solution containing polypropylene carbonate

It is preferable that methocarbon microbead carbon has a mean particle size satisfying a range from 6  $\mu\text{m}$  to 25  $\mu\text{m}$ . As the mean particle size of the methocarbon microbead carbon is reduced, the overvoltage in the electrode reaction can be reduced. As a result, the output characteristics of the battery can be improved. To raise the electrode filling density, it is advantage to enlarge the mean particle size. Therefore, it is preferable that methocarbon microbead carbon having a mean particle size satisfying the range from 6  $\mu\text{m}$  to 25  $\mu\text{m}$  is employed.

Fig. 5 shows a state where the gel electrolyte layer 4 to be described later has been formed on the negative-electrode active material layer 3a of the negative electrode 3.

The gel electrolyte layer 4 contains electrolyte salt, matrix polymers and swelling solvent which serves as a plasticizer.

The electrolyte salt may be any one of  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiN}(\text{CF}_3\text{SO}_3)_2$  and  $\text{C}_4\text{F}_9\text{SO}_3\text{Li}$  which may be employed solely or their combination

may be employed. In particular, it is preferable that  $\text{LiPF}_6$  is employed from a viewpoint of obtaining satisfactory ion conductivity.

The matrix polymer must have an ion conductivity of 1 mS/cm or higher at room temperature as a sole polymer or in the form of a gel electrolyte. When the foregoing ion conductivity is realized, the chemical structure of the matrix polymer is not limited. The matrix polymer is exemplified by polyvinylidene fluoride, polyacrylonitrile, polyethylene oxide, a polysiloxane compound, a polyphosphagen compound, polypropylene oxide, polymethylmethacrylate, polymethacrylonitrile and a polyether compound. Also a material obtained by copolymerizing another polymer with the foregoing polymer may be employed. From a viewpoint of realizing the chemical stability and ion conductivity, a material is employed in the copolymerization ratio of polyvinylidene fluoride and polyhexafluoropropylene in terms of the weight ratio is lower than 8 %.

The swelling solvent may be nonaqueous solvent exemplified by ethylene carbonate, polypropylene carbonate,  $\gamma$ -butyrolactone, acetonitrile, diethylether, diethyl carbonate, dimethyl carbonate, 1, 2-dimethoxyethane, dimethylsulfoxide, 1, 3-dioxolane, methylsulfonate, 2-methyltetrahydrofuran, tetrahydrofuran, sulfolane, 2, 4-difluoroanisole and vinylene carbonate. The foregoing material may be employed solely or their mixture may be employed.

In particular, it is preferable that a material, such as ethylene carbonate, propylene carbonate or  $\gamma$ -butyrolactone, having a relatively wide potential window, is

employed. Note that the potential window is a potential region in which the solvent is able to stably present.

When 2, 4-difluoroanisole or vinylene carbonate is added in a quantity satisfying a range from 0.5 % to 5 % of the overall weight of the solvent, the characteristics of the battery can sometimes be improved.

It is preferable that the gel electrolyte layer 4 has a structure that the mixture ratio of the matrix polymer and the swelling solvent is such that the matrix polymer and swelling solvent is not lower than 1:5 or higher nor higher than 1:10. When the quantity of the swelling solvent is smaller than five times the quantity of the matrix polymer, the electrolytic solution component in the gel electrolyte is too small. Thus, the ion conductivity of the gel electrolyte layer 4 deteriorates. When the quantity of the swelling solvent is larger than 10 times the quantity of the matrix polymer, the gel electrolyte becomes brittle. Thus, satisfactory liquid holding performance of the matrix polymer cannot be obtained.

When the mixture ratio of the matrix polymer and the swelling solvent satisfies the foregoing range, the liquid holding performance of the matrix polymer can be maintained. Moreover, the ion conductivity of the gel electrolyte layer 4 can be maintained.

It is preferable that the thickness of the gel electrolyte layer 4 is not smaller than 5  $\mu\text{m}$  nor larger than 19  $\mu\text{m}$ . When the thickness of the gel electrolyte layer 4 is smaller than 5  $\mu\text{m}$ , a quantity of gel required to cause the electrode reaction to proceed



smoothly cannot easily be obtained. When the thickness of the gel electrolyte layer 4 is larger than  $19\text{ }\mu\text{m}$ , the distance between the positive electrode 2 and the negative electrode 3 is elongated. As the distance between the two electrodes is elongated, the energy density of the battery and the output characteristics of the same deteriorate excessively. Therefore, the thickness of the gel electrolyte layer 4 is made to be not smaller than  $5\text{ }\mu\text{m}$  nor larger than  $19\text{ }\mu\text{m}$ . Thus, deterioration in the energy density of the battery and that of the output characteristics can be prevented during the reaction of the electrode.

The separator 5 disposed between the positive electrode 2 and the negative electrode 3 prevents occurrence of short circuit caused from the physical contact between the positive electrode 2 and the negative electrode 3.

The thickness of the separator 5 according to this embodiment satisfies a range not smaller than  $5\text{ }\mu\text{m}$  nor larger than  $15\text{ }\mu\text{m}$ . When the thickness of the separator 5 is smaller than  $5\text{ }\mu\text{m}$ , the separator 5 cannot easily be handled during a process for manufacturing the battery. As a result, the manufacturing yield of the gel electrolyte battery 1 deteriorates. When the thickness of the separator 5 is larger than  $15\text{ }\mu\text{m}$ , the internal resistance of the gel electrolyte battery 1 is raised excessively. What is worse, the energy density loss is enlarged. Therefore, the thickness of the separator 5 is made to satisfy the range not smaller than  $5\text{ }\mu\text{m}$  nor larger than  $15\text{ }\mu\text{m}$ . Hence it follows that deterioration in the manufacturing yield of the gel electrolyte battery 1, increase in the internal resistance and enlargement of the energy density loss can be prevented.

The vacancy ratio of the separator 5 according to this embodiment satisfies a range not lower than 25 % nor higher than 60 %. When the vacancy ratio of the separator 5 is lower than 25 %, the internal resistance of the gel electrolyte battery 1 is excessively raised to obtain predetermined output characteristics. When the vacancy ratio of the separator 5 is higher than 60 %, satisfactory mechanical strength cannot easily be realized. Therefore, the vacancy ratio of the separator 5 is made to satisfy a range not lower than 25 % nor higher than 60 %. Thus, the mechanical strength of the separator 5 can be maintained without any rise in the internal resistance of the gel electrolyte battery 1.

The separator 5 according to this embodiment has a shutdown effect when the temperature of the battery satisfies a range not lower than 100°C nor higher than 160°C. To obtain the shutdown effect when the temperature of the battery satisfies the range not lower than 100°C nor higher than 160°C, the melting points of the materials of the separator 5 must satisfy a range not lower than 100°C nor higher than 160°C. Since the separator 5 is disposed between electrodes, the separator 5 must have electro-chemical stability.

The description that the "shutdown effect is obtained when the temperature of the separator 5 satisfies the range not lower than 100°C nor higher than 160°C" means a fact that the internal impedance of the battery is enlarged as compared with that realized at room temperature by two digits or more when the temperature of the battery satisfies the range not lower than 100°C nor higher than 160°C.

As a material which satisfies the foregoing conditions, a polyolefine polymer is a representative material which is exemplified by polyethylene or polypropylene. In particular, it is preferable that the separator 5 is made of polyethylene. As an alternative to the polyolefine polymer, resin of a type having chemical stability with respect to the gel electrolyte may be employed such that the resin is copolymerized or blended with polyethylene or polypropylene.

As described above, the separator 5 has the thickness satisfying the range not smaller than  $5\text{ }\mu\text{m}$  nor larger than  $15\text{ }\mu\text{m}$ , the vacancy ratio satisfying the range not lower than 25 % nor higher than 60 % and the shutdown effect when the temperature satisfies the range not lower than  $100^{\circ}\text{C}$  nor higher than  $160^{\circ}\text{C}$ . Thus, the energy density of the gel electrolyte battery 1 can be raised and safety can be improved.

Moreover, the inventor of the present invention has energetically studied the relationship between the physical properties of the separator 5 and the characteristics of the battery. As a result, the following fact has been detected: it is preferable that the separator 5 having the thickness satisfying the range not smaller than  $5\text{ }\mu\text{m}$  nor larger than  $15\text{ }\mu\text{m}$  and the vacancy ratio satisfying the range not lower than 25 % nor higher than 60 % has breaking strength lower than  $1650\text{ kg/cm}^2$  and breaking ductility of 135 % or higher. When the breaking strength and the breaking ductility of the separator 5 cannot satisfy the foregoing ranges, the separator 5 cannot easily be handled in the process for manufacturing the gel electrolyte battery 1. Thus, the manufacturing yield of the gel electrolyte battery 1 deteriorates. What is worse,

satisfactory characteristics of the battery cannot be obtained. Therefore, employment of the separator 5 having the breaking strength lower than  $1650 \text{ kg/cm}^2$  and the breaking ductility of 135 % or higher enables deterioration in the manufacturing yield of the gel electrolyte battery 1 to be prevented. Thus, satisfactory characteristics of the gel electrolyte battery 1 can be obtained.

A tensile test of the separator 5 is performed as follows to evaluate the breaking strength and the breaking ductility of the separator 5 will now be described.

A test piece of the separator 5 in the form of substantially a  $30 \text{ mm} \times 70 \text{ mm}$  rectangular shape was obtained by cutting. Then, a cellophane tape having a width of 10 mm is applied to each of two lengthwise ends of the test piece.

Then, the obtained test piece is sufficiently clamped in a sample clamping portion of a tensile testing machine. The tensile testing machine may be, for example, model NO. 1310f manufactured by Aiko. The portion of the test piece to be clamped by the sample clamping portion is a portion which has been reinforced with the cellophane tape. That is, the portion of the test piece having a length of 50 mm except for the two-end reinforced portions each having the length of 10 mm is subjected to the tensile test.

In the foregoing state, a fact that the test piece is placed perpendicular to the testing machine table is confirmed. Then, the tensile test is started. The tensile strength is 40 mm per minute. Data about the load and the ductility ratio are recorded in a personal computer through an A/D conversion board. In accordance with obtained

data, the breaking strength and the breaking ductility are calculated. The load with which the test piece has been broken is employed as the breaking strength. The length (mm) of the test piece immediately before the test piece is broken is measured to obtain the breaking ductility (%) by using Equation (1).

$$\text{Breaking Ductility} = 100 \times (\text{Length of Test Piece Immediately Before Breakage} / 50) \dots (1)$$

The above-mentioned means is performed so that the separator 5 according to this embodiment is arranged to have the breaking strength which is lower than 1650 kg/cm<sup>2</sup> and the breaking strength of 135 % or higher. When the separator 5 satisfying the foregoing mechanism characteristics is employed, deterioration in the manufacturing yield of the gel electrolyte battery 1 can be prevented. Moreover, satisfactory characteristics of the battery can be obtained.

As described above, the separator 5 is employed which has the thickness not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$ , the vacancy ratio not lower than 25 % nor higher than 60 %, the breaking strength lower than 1650 kg/cm<sup>2</sup> and the breaking ductility of 135 % or higher. Thus, a high energy density and safety of the gel electrolyte battery 1 can be realized.

One of objects of the separator 5 is to prevent short circuit caused from the physical contact between the positive electrode 2 and the negative electrode 3. The

size of the separator 5 is determined to depend on the sizes of the positive electrode 2 and the negative electrode 3 and the shapes of the battery elements. That is, the opposite electrodes must completely be insulated from each other by the separator 5. Moreover, the terminal of the electrode and the electrode must be insulated from each other by the separator 5. To realize the foregoing state, the size of the separator 5 must be larger than the overall size of each of the positive electrode 2 and the negative electrode 3.

A fact that the separator 5 according to this embodiment has a fine structure which is a so-called fibril structure as shown in Fig. 6 has been detected from experiments. Fig. 6 is a photograph of the fine structure of the wound electrode 6 taken by an electronic microscope at a magnification of 50,000 times.

As a means for obtaining the separator 5 having the fibril structure, a plurality of methods may be employed. An example of the method will now be described.

Initially, molten liquid of low-volatile solvent (good solvent with respect to a polyolefine composition) is supplied to an extruder including a molten polyolefine composition so as to be kneaded. Thus, high-concentration solution of the polyolefine composition having a uniform concentration is prepared.

The polyolefine is exemplified by polyethylene and polypropylene. It is preferable that polyethylene is employed. The low-volatile solvent may be low-volatile aliphatic hydrocarbon or cyclic hydrocarbon, such as nonane, decane, decalin, p-xylene, undecane or liquid paraffin.

It is preferable that the mixture ratio of the polyolefine composition and the low-volatile solvent satisfies a range not smaller than 10 parts by weight nor larger than 80 parts by weight with respect to 100 parts by weight which is the total quantity of the two materials, preferably a range not smaller than 15 parts by weight nor larger than 70 parts by weight. When the quantity of the polyolefine composition is smaller than 10 parts by weight, swelling or neck-in occurs excessively at the outlet opening of the dice. In the foregoing case, a required sheet cannot easily be formed. When the quantity of the polyolefine composition is larger than 80 parts by weight, uniform solution cannot easily be prepared. Therefore, the ratio of polyolefine is made to satisfy the range not smaller than 10 parts by weight nor larger than 80 parts by weight. Thus, the preparation of uniform solvent and formation of the sheet can easily be performed.

Heated solution of the polyolefine composition is extruded through the dice so that a sheet of the polyolefine composition solution is obtained which is then cooled. Thus, a gel sheet is obtained. The cooling process is performed until a temperature not higher than the gelling temperature is realized. As a cooling method, the following methods may be employed: a method with which direct contact with cold air, cooling water or another cooling medium is established; or a method with which the contact with a roll cooled with a refrigerant is established.

The polyolefine composition solution extruded from the dice may be taken up at a take-up ratio satisfying a range not lower than 1 nor higher than 10, preferably a

range not lower than 1 nor higher than 5. When the take-up ratio is 10 or higher, great neck-in takes place and breakage easily occurs. When the take-up ratio is made to satisfy the range not lower than 1 nor higher than 10, neck-in and breakage of the gel sheet can be prevented.

Then, the obtained gel sheet is heated so as to be oriented at a predetermined magnification so that an oriented film is obtained. The gel sheet is oriented by a usual tenter method, a roll method, a milling method or a method of combination of the foregoing methods. It is preferable that a biaxial orientation method is employed. The biaxial orientation method may be either of simultaneous orientation in the lengthwise and breadthwise directions or a sequential method. In particular, it is preferable that the simultaneous biaxial orientation is employed.

It is preferable that the gel sheet is oriented at a temperature of the melting point of the polyolefine composition + 10°C or lower. More preferably, the orienting temperature satisfies a range not lower than the crystal dispersion temperature of the polyolefine composition and lower than the melting point of the same. When the orienting temperature is higher than the melting point of the polyolefine composition + 10°C, resin is undesirably melted. In the foregoing case, effective orientation of molecules cannot be realized. When the orienting temperature is lower than the crystal dispersing temperature, the resin cannot sufficiently be softened. In the foregoing case, breakage easily occurs in the orienting process and, therefore, orientation at a high magnification cannot be performed. When the orienting temperature of the gel



sheet is made to satisfy the foregoing range, uniform and high-magnification orientation can be performed. Moreover, orientation of the molecule chains can effectively be performed.

The obtained oriented film is cleaned with volatile solvent to remove residual low-volatile solvent. The volatile solvent for use in the cleaning process may be basic hydrocarbon, such as pentane, hexane or heptane; hydrogen fluoride, such as ethane trifluoride; or ether, such as diethylether or dioxane. The foregoing material is employed solely or the foregoing materials may be mixed. The solvent for cleaning the oriented film may properly be selected to be adaptable to the low-volatile solvent for use to dissolve the polyolefine composition.

The oriented film may be cleaned by a method with which the oriented film is immersed in the solvent to extract low-volatile solvent left in the oriented film; a method for showering the solvent to the oriented film; or their combination. The oriented film is cleaned until the quantity of the low-volatile solvent left in the oriented film is smaller than one part by weight.

Finally, the solvent used to clean the oriented film is dried so as to be removed. The solvent is dried by heating or air spraying. After the foregoing process has been completed, the separator 5 according to this embodiment can be obtained. The thus-obtained separator 5 has the fibril structure as shown in Fig. 6.

The gel electrolyte battery 1 according to this embodiment and incorporating the foregoing separator 5 is manufactured as follows.

The positive electrode 2 is manufactured as follows: positive-electrode mix containing the positive-electrode active material and a binder is uniformly applied to the surface of metal foil, such as aluminum foil, which is formed into the positive-electrode collector 2b, and then the positive-electrode mix is dried. Thus, the positive-electrode active material layer 2a is formed so that a positive electrode sheet is manufactured. The binder of the positive-electrode mix may be a known binder. Note that a known additive may be added to the positive-electrode mix.

Then, the gel electrolyte layer 4 is formed on the positive-electrode active material layer 2a of the positive electrode sheet. To form the gel electrolyte layer 4, a first step is performed so that electrolyte salt is dissolved in the nonaqueous solvent. Thus, nonaqueous electrolytic solution is prepared. The matrix polymer is added to the nonaqueous electrolytic solution, and then the solution is sufficiently stirred to dissolve the matrix polymer. As a result, sol electrolyte solution is prepared.

Then, the electrolyte solution in a predetermined quantity is applied to the surface of the positive-electrode active material layer 2a. Then, the positive-electrode active material layer 2a is cooled at room temperature so as to gel the matrix polymer. Hence it follows that the gel electrolyte layer 4 is formed on the positive-electrode active material layer 2a.

Then, the positive electrode sheet having the gel electrolyte layer 4 formed thereon is cut to obtain elongated members. An aluminum lead wire is welded to a portion of the positive-electrode collector 2b in which the positive-electrode active

material layer 2a is not formed so that the positive-electrode terminal 8 is formed. Thus, the elongated positive electrode 2 having the gel electrolyte layer 4 formed thereon can be obtained.

The negative electrode 3 is formed as follows: a negative-electrode mix containing a negative-electrode active material and a binder is uniformly applied to metal foil, such as copper foil, which is formed into the negative-electrode collector 3b. Then, the metal foil is dried so that a negative electrode sheet having the negative-electrode active material layer 3a formed thereon is manufactured. The binder may be a known binder. Note that a known additive may be added to the negative-electrode mix.

Then, the gel electrolyte layer 4 is formed on the negative-electrode collector 3b. To form the gel electrolyte layer 4, a process similar to the foregoing process is performed so that electrolyte solution prepared similarly to the foregoing process is applied to the negative-electrode active material layer in a predetermined quantity. Then, the negative-electrode active material layer is dried at room temperature to gel the matrix polymer. As a result, the gel electrolyte layer 4 is formed on the negative-electrode collector 3b.

Then, the negative electrode sheet having the gel electrolyte layer 4 formed thereon is cut to obtain elongated members. A lead wire constituted by, for example, nickel, is welded to a portion of the negative-electrode collector 3b in which the negative-electrode active material layer 3a is not formed. Thus, the negative-electrode

terminal 9 is formed. Thus, the elongated negative electrode 3 having the gel electrolyte layer 4 formed thereon can be obtained.

The surfaces of the thus-manufactured elongated positive electrode 2 and the negative electrode 3 each having the gel electrolyte layer 4 formed thereon are disposed opposite to each other. The separator 5 is inserted between the positive electrode 2 and the negative electrode 3 to bond and press the laminate. Thus, an electrode laminate is obtained. The electrode laminate is wound in the lengthwise direction so that the wound electrode 6 is obtained.

Finally, the wound electrode 6 is sandwiched by the casing film 7. Then, the resin film 10 is disposed in each of the portion in which the positive-electrode terminal 8, the negative-electrode terminal 9 and the casing film 7 overlap. Then, the outer periphery of the casing film 7 is sealed. Then, the positive-electrode terminal 8 and the negative-electrode terminal 9 are sandwiched in the sealing opening of the casing film 7. Moreover, the wound electrode 6 is hermetically enclosed in the casing film 7. In a state where the wound electrode 6 is packed in the casing film 7, the wound electrode 6 is subjected to heat treatment. Thus, the gel electrolyte battery 1 can be manufactured.

When the wound electrode 6 is packed in the casing film 7, the resin film 10 is disposed in each of the contact portions between the casing film 7 and the positive-electrode terminal 8 and between the casing film 7 and the negative-electrode terminal 9. Therefore, occurrence of short circuit caused from burrs of the casing film

7 or the like can be prevented. Moreover, the adhesiveness between the casing film 7 and the positive-electrode terminal 8 and between the casing film 7 and the negative-electrode terminal 9 can be improved.

The resin film 10 may be constituted by a material which must have adhesiveness to the positive-electrode terminal 8 and the negative-electrode terminal 9. When the material has the foregoing adhesiveness, the material is not limited. It is preferable that any one of polyethylene, polypropylene, denatured polyethylene, denatured polypropylene, their copolymers and polyolefine resin is employed. It is preferable that the thickness of the resin film 10 realized before heat welding satisfies a range from 20  $\mu\text{m}$  to 300  $\mu\text{m}$ . When the thickness of the resin film 10 is smaller than 20  $\mu\text{m}$ , handling deteriorates. When the thickness is larger than 300  $\mu\text{m}$ , water easily penetrates the resin film 10. As a result, the airtightness in the battery cannot easily be maintained.

In the foregoing embodiment, the elongated positive electrode 2 and the elongated negative electrode 3 are laminated. Then, the laminate is wound in the lengthwise direction to form the wound electrode 6. The present invention is not limited to the foregoing structure. The present invention may be applied to a structure with which a rectangular positive electrode 2 and a rectangular negative electrode 3 are laminated to form the electrode laminate or a structure in which the electrode laminate is alternately folded.

In the foregoing embodiment, the electrolyte to be interposed between the

positive electrode 2 and the negative electrode 3 is the gel electrolyte containing swelling solvent. The present invention is not limited to the foregoing structure. The present invention may be applied to a structure in which a solid electrolyte which does not contain the swelling solvent is employed.

The solid electrolyte must have ion conductivity of 1 mS/cm or higher at room temperature. When the solid electrolyte has the foregoing characteristic, its chemical structure is not limited. The solid electrolyte of the foregoing type is exemplified by an organic solid electrolyte obtained by dissolving inorganic salt in any one of polyvinylidene fluoride, polyacrylonitrile, polyethylene oxide, a polysiloxane compound, a polyphosphagen compound, polypropylene oxide, polymethylmethacrylate, polymethacrylonitrile or a polyether compound, an ion-conductive ceramic material or ion-conductive glass.

The shape of the gel electrolyte battery 1 according to this embodiment is not limited. For example, a cylindrical shape, a rectangular shape, a coin shape or the like may be employed. The present invention may be applied to both of a primary battery and a secondary battery.

#### Second Embodiment

An example of the structure of a gel electrolyte battery 20 according to this embodiment is shown in Figs. 7 and 8. The gel electrolyte battery 20 incorporates an elongated positive electrode 21; an elongated negative electrode 22 disposed opposite to the positive electrode 21; a gel electrolyte layer 23 formed on each of the positive

electrode 21 and the negative electrode 22; and a separator 24 disposed between the positive electrode 21 having the gel electrolyte layer 23 formed thereon and the negative electrode 22 having the gel electrolyte layer 23 formed thereon.

The gel electrolyte battery 20 incorporates the positive electrode 21 having the gel electrolyte layer 23 formed thereon and the negative electrode 22 having the gel electrolyte layer 23 formed thereon. The positive electrode 21 and the negative electrode 22 are laminated through the separator 24 and wound in the lengthwise direction so that a wound electrode 25 structured as shown in Fig. 9 is formed. The wound electrode 25 is covered with a casing film 26 and constituted by an insulating material so that the wound electrode 25 is sealed by the casing film 26. A positive-electrode terminal 27 is connected to the positive electrode 21, while a negative-electrode terminal 28 is connected to the negative electrode 22. The positive-electrode terminal 27 and the negative-electrode terminal 28 are sandwiched in a sealing opening which is the outer periphery of the casing film 26. The portions in which the positive-electrode terminal 27 and the negative-electrode terminal 28 are in contact with the casing film 26 are provided with resin films 29.

As shown in Fig. 10, the positive electrode 21 incorporates a positive-electrode active material layer 21a containing a positive-electrode active material and formed on a positive electrode collector 21b. The positive electrode collector 21b may be constituted by metal foil, such as aluminum foil.

The positive-electrode active material may be a material which permits

implantation and separation of positive ions. Ions above are exemplified by Li ions. Specifically, the positive-electrode active material is exemplified by  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$ . Two or more types of transition metal elements may be employed as well as use of a sole transition metal element. Specifically,  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$  or the like may be employed.

The positive-electrode active material layer 21a is formed as follows: the foregoing positive-electrode active material, a carbon material serving as a conductive material and polyvinylidene fluoride serving as a binder are mixed. Then, N-methylpyrrolidone serving as solvent is added so that slurry is prepared. The obtained slurry is uniformly applied to the surface of the aluminum foil which is formed into the positive electrode collector by a doctor blade method. Then, the aluminum foil is dried at high temperatures so that the N-methylpyrrolidone is removed.

As for the mixture ratio of the positive-electrode active material, the conductor, the binder and N-methylpyrrolidone, the mixture ratio is not limited. The necessity lies in that slurry is realized in which mixture is uniformly dispersed.

Fig. 10 shows a state where a gel electrolyte layer 23 to be described later is formed on the positive-electrode active material layer 21a of the positive electrode 21.

As shown in Fig. 11, the negative electrode 22 incorporates a negative-electrode active material layer 22a containing a negative-electrode active material and formed on the negative electrode collector 22b. The negative electrode collector 22b is



constituted by, for example, metal foil, such as copper foil.

The negative-electrode active material may be a material which permits implantation and separation of Li and which is exemplified by graphite, non-graphitizable carbon or graphitizable carbon.

The negative-electrode active material layer 22a is formed as follows: the foregoing negative-electrode active material and polyvinylidene fluoride serving as the binder are mixed with each other. Then, N-methylpyrrolidone serving as solvent is added to prepare slurry. The obtained slurry is uniformly applied to the surface of copper foil which is formed into a negative-electrode collector by the doctor blade method. Then, the copper foil is dried at high temperatures to remove N-methylpyrrolidone. Thus, the negative-electrode active material layer 22a is formed.

The mixture ratio of the negative-electrode active material, the binder and N-methylpyrrolidone is determined to prepare slurry in which the mixture is uniformly dispersed. Therefore, the mixture ratio is not limited. The description "permitting insertion and separation of Li" is not limited to insertion and removal of Li with respect to the inside portion of the crystal structure. When charge and discharge are permitted in a case of a constituted battery, a determination is made that implantation and separation can be performed. The negative electrode is exemplified by a Li negative electrode and a Li-Al alloy negative electrode.

Fig. 11 shows a state where a gel electrolyte layer 23 to be described later has been formed on the negative-electrode active material layer 22a of the negative

electrode 22.

The gel electrolyte layer 23 contains electrolyte salt, a matrix polymer and solvent serving as a plasticizer.

The matrix polymer must have compatibility with the solvent. The material is exemplified by polyacrylonitrile, a polyethylene oxide polymer, polyvinylidene fluoride, a copolymer of polyvinylidene fluoride and hexafluoropropylene, styrene-butadiene rubber and polymethylmethacrylate. Two or more types of matrix polymers may be employed as well as use only one type. A polymer which is not included in the foregoing examples, which has compatibility with the solvent and which is formed into gel may be employed.

The solvent is solvent which can be dispersed in the matrix polymer. Non-proton solvent is exemplified by ethylene carbonate, polypropylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone, diethyl carbonate, dimethyl carbonate, ethylmethyl carbonate and dimethoxyethane. Only one type of the foregoing materials may be employed as the solvent or two or more types of the foregoing materials may be employed.

The electrolyte salt must dissolved in the foregoing solvent. Cation is exemplified by alkali metal and alkaline earth metal. Anion is exemplified by  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$  and  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ . The concentration of the electrolyte salt must be a concentration with which the electrolyte salt can be dissolved in the solvent.

It is preferable that the thickness of the gel electrolyte layer 23 satisfies a range from 5  $\mu\text{m}$  or larger to 15  $\mu\text{m}$  or smaller. When the thickness of the gel electrolyte layer 23 is smaller than 5  $\mu\text{m}$ , short circuit caused from contact between the positive electrode and the negative electrode cannot sufficiently be prevented. When the thickness of the gel electrolyte layer 23 is larger than 15  $\mu\text{m}$ , resistance against a large load deteriorates and the volume energy density is lowered.

The separator 24 is disposed between the positive electrode 2 and the negative electrode 3 to prevent short circuit caused from the physical contact between the positive electrode 2 and the negative electrode 3. The separator 24 according to this embodiment is constituted by a composite material of polyethylene and polypropylene obtained by adding polypropylene to polyethylene. When the separator 24 is constituted by the composite material of polyethylene and polypropylene, only the melt-down temperature can be raised while maintaining the shutdown temperature of the separator 24 which is similar to that of the polyethylene separator.

Specifically, it is preferable that the melt-down temperature of the separator 24 is higher than the melt-down temperature of the polyethylene separator by a degree satisfying a range from 10°C or higher to 30°C or lower. The melt-down temperature is a temperature at which the shutdown separator 24 is melted and broken.

When the melt-down temperature of the separator 24 is higher than the melt-down temperature of the polyethylene separator by a degree satisfying a range lower than 10°C, the effect of the present invention to raise the melt-down

temperature cannot satisfactorily be obtained. The reason why the melt-down temperature of the separator 24 is higher than the melt-down temperature of the polyethylene separator by a degree satisfying a range not higher than 30°C will now be described. That is, the difference between the melt-down temperature of the polypropylene separator and that of the polyethylene separator is about 30°C.

It is preferable that the thickness of the separator 24 according to this embodiment satisfies a range from 5  $\mu\text{m}$  or larger to 15  $\mu\text{m}$  or smaller. When the thickness of the separator 24 is smaller than 5  $\mu\text{m}$ , the separator 24 cannot easily be handled when the battery is manufactured. Thus, the manufacturing yield of the battery deteriorates. When the thickness of the separator 24 is larger than 15  $\mu\text{m}$ , the internal resistance of the battery is raised. What is worse, the energy density loss is enlarged undesirably. Therefore, the thickness of the separator 24 is made to satisfy the range from 5  $\mu\text{m}$  or larger to 15  $\mu\text{m}$  or smaller. Thus, deterioration in the manufacturing yield of the battery, rising of the internal resistance of the battery and the energy density loss can be prevented.

It is preferable that the vacancy ratio of the separator 24 is not lower than 25 % nor higher than 60 %. When the vacancy ratio of the separator 24 is lower than 25 %, the internal resistance of the battery is raised excessively to obtain required output characteristics. When the vacancy ratio of the separator 24 is higher than 60 %, satisfactory mechanical strength of the separator 24 cannot be obtained. Therefore, the vacancy ratio of the separator 24 is made to satisfy the range not lower than 25 %

nor higher than 60 %. Thus, the mechanical strength of the separator 24 can be maintained without any increase in the internal resistance of the battery. Therefore, the vacancy ratio of the separator 24 is made to satisfy the range not lower than 25 % nor higher than 60 %. Thus, the mechanical strength of the separator 24 can be maintained without any increase in the internal resistance of the battery.

As described above, the separator 24 according to this embodiment is manufactured, for example, as follows. Note that the method of manufacturing the separator 24 is not limited to the following specific values. Also the mixture ratio of the polyethylene and polypropylene which constitute the separator 24 is not limited to the following value.

Initially, 0.375 part by weight of oxidation inhibitor is added to 100 parts by weight of a polyolefine mixture composed of 20 wt% of ultra-high molecular weight polyethylene (UHMWPE) having a weight average molecular weight  $M_w$  of  $2.5 \times 10^6$ , 30 wt% of high-density polyethylene (HDPE) having a weight average molecular weight  $M_w$  of  $3.5 \times 10^5$  and 50 wt% of polypropylene having a weight average molecular weight  $M_w$  of  $5.1 \times 10^5$  so that a polyolefine composition is prepared.

Then, 30 parts by weight of the polyolefine composition were introduced into a biaxial extruder (having a diameter of 58 mm,  $L/D = 42$  and strong kneading type). Moreover, 70 parts by weight of liquid paraffin were supplied through a side feeder so as to be melted and kneaded at 200 rpm so that polyolefine solution is prepared in the extruder.

Then, the polyolefine solution is extruded from a T-die disposed at the leading end of the extruder at 190°C so as to be wound around a cooling roll. Thus, a gel sheet is molded. Then, the gel sheet is simultaneous double-axis oriented at 115°C to obtain a 5 × 5 oriented film. The obtained oriented film is cleaned with methylene chloride to extract and remove liquid paraffin. Then, the oriented film is dried and subjected to heat treatment. Thus, a fine-porous separator 24 constituted by a composite material of polyethylene and polypropylene is obtained.

The separator 24 according to this embodiment constituted by the composite material of polyethylene and polypropylene may be structured by bonding each of a separator 24a constituted by polyethylene and a separator 24b constituted by polypropylene to each other as shown in Fig. 12. When the separator 24a constituted by polyethylene and the separator 24b constituted by polypropylene are bonded to each other, the melt-down temperature of the separator 24 can be raised to the melt-down temperature of the polypropylene while maintaining the shutdown temperature of the separator 24 which is the temperature of polyethylene.

The reason why each of the separator 24a constituted by polyethylene and the separator 24b constituted by polypropylene are bonded to each other will now be described. When three or more separators are overlaid, the thickness of the separator is enlarged excessively to prevent increase in the internal resistance of the battery. Thus, there arises a problem in that the energy density loss is enlarged undesirably. Therefore, each of the separator 24a constituted by polyethylene and the separator 24b

constituted by polypropylene are bonded to each other so that the thickness of the separator is reduced as much as possible. Thus, a maximum effect can be obtained.

When the separator 24 is formed into the foregoing bonded structure, it is preferable that the thickness of each of the separator 24a constituted by polyethylene and the separator 24b constituted by polypropylene satisfies a range not smaller than  $2.5\text{ }\mu\text{m}$  nor larger than  $7.5\text{ }\mu\text{m}$ . Moreover, it is preferable that the total thickness of the two separators satisfies a range not smaller than  $5\text{ }\mu\text{m}$  nor larger than  $15\text{ }\mu\text{m}$ . When the thickness of the separator 24 is smaller than  $5\text{ }\mu\text{m}$ , the separator 24 cannot easily be handled when the battery is manufactured. Thus, the manufacturing yield of the battery deteriorates. When the thickness of the separator 24 is larger than  $15\text{ }\mu\text{m}$ , the internal resistance of the battery is raised excessively. What is worse, there arises a problem in that the energy density loss is enlarged. Therefore, the thickness of the separator 24 is made to satisfy the range not smaller than  $5\text{ }\mu\text{m}$  nor larger than  $15\text{ }\mu\text{m}$ . Thus, deterioration in the manufacturing yield of the battery, increase in the internal resistance of the battery and great energy density loss can be prevented.

The separator 24 according to this embodiment structured as described must have a width larger than the width of each of the positive electrode 22 and the negative electrode 23, as shown in Fig. 13. When the positive electrode 22, the negative electrode 23 and the separator 24 are overlaid and wound, deviation of the positive electrode 22, the negative electrode 23 and the separator 24 sometimes occurs. Assuming that the amounts of the widthwise directional deviation are  $L_1$  and  $L_2$  when

the positive electrode 22, the negative electrode 23 and the separator 24 have been overlaid as shown in Fig. 13, the positive electrode 22 and the negative electrode 23 are brought into contact with each other when  $L_1 < 0$  or  $L_2 < 0$ . That is, when the end of the separator 24 is inner than the end of the positive electrode 22 or the negative electrode 23, the contact occurs. As a result, internal short circuit occurs, causing the manufacturing yield of the battery to deteriorate.

Therefore, when deviation takes place in a process for overlaying and winding the positive electrode 22, the negative electrode 23 and the separator 24, occurrence of the contact between the positive electrode 22 and the gel electrolyte layer 23 must be prevented. Thus, the width of the separator 24 must somewhat be larger than the width of each of the positive electrode 22 and the negative electrode 23. In a case where the width of the separator 24 is excessively enlarged, the energy density of the battery is lowered. Therefore, the width of the separator 24 must be determined in such a manner that  $L_1 > 0.5$  mm,  $L_2 > 0.5$  mm and  $L_1 + L_2 < 4$  mm as shown in Fig. 13. When the separator 24 has the foregoing width, occurrence of internal short circuit caused from the positive electrode 22 and the gel electrolyte layer 23 can be prevented in case of deviation among the positive electrode 22, the negative electrode 23 and the separator 24. As a result, deterioration in the manufacturing yield can be prevented.

The gel electrolyte battery 20 incorporating the above-mentioned separator 24 and according to this embodiment is manufactured as follows.

Initially, the positive electrode 21 is manufactured as follows: a



positive-electrode mix containing a positive-electrode active material and a binder is uniformly applied to the surface of metal foil, such as aluminum foil, which is formed into the positive electrode collector 21b. Then, the metal foil is dried so that the positive-electrode active material layer 21a is formed. Thus, a sheet of the positive electrode 2 is manufactured. The binder of the positive-electrode mix may be a known binder. Note that a known additive may be added to the positive-electrode mix.

Then, the gel electrolyte layer 23 is formed on the positive-electrode active material layer 21a of the positive electrode sheet. To form the gel electrolyte layer 23, electrolyte salt is dissolved in nonaqueous solvent to prepare nonaqueous electrolytic solution. The matrix polymer is added to the nonaqueous electrolytic solution, and then the solution is sufficiently stirred so as to dissolve the matrix polymer. Thus, sol electrolyte solution is prepared.

Then, the electrolyte solution is applied to the surface of the positive-electrode active material layer 21a in a predetermined quantity. Then, the positive-electrode active material layer 21a is cooled at room temperature to gel the matrix polymer. Thus, the gel electrolyte layer 23 is formed on the positive-electrode active material layer 21a.

Then, the positive electrode sheet having the gel electrolyte layer 23 formed thereon is cut to obtain an elongated member. Then, a lead wire constituted by, for aluminum, is welded to a portion of the positive electrode collector 21b in which the positive-electrode active material layer 21a is not formed so that the positive-electrode

terminal 27 is formed. Thus, an elongated positive electrode 21 having the gel electrolyte layer 23 formed thereon can be obtained.

The negative electrode 22 is manufactured as follows: a negative-electrode mix containing a negative-electrode active material and a binder is uniformly applied to metal foil, such as copper foil, which is formed into the negative electrode collector 22b. Then, the metal foil is dried so that the negative-electrode active material layer 22a is formed. Thus, a negative electrode sheet is manufactured. The binder of the negative-electrode mix may be a known binder. Note that a known additive may be added to the negative-electrode mix.

Then, the gel electrolyte layer 4 is formed on the negative electrode collector 22b of the negative electrode sheet. To form the gel electrolyte layer 23, electrolyte solution prepared similarly to the foregoing process is applied to the negative-electrode active material layer in a predetermined quantity. Then, the negative-electrode active material layer is cooled at room temperature so as to gel the matrix polymer. As a result, the gel electrolyte layer 23 is formed on the negative electrode collector 22b.

Then, the negative electrode sheet having the gel electrolyte layer 4 formed thereon is cut to have an elongated member. Then, a lead wire constituted by, for example, nickel, is welded to a portion of the negative electrode collector 22b in which the negative-electrode active material layer 22a is not formed so that the negative-electrode terminal 28 is formed. Thus, the elongated negative electrode 3 having the gel electrolyte layer 23 formed thereon can be obtained.

The surfaces of the thus-manufactured elongated positive electrode 21 and the negative electrode 22 on each of which the gel electrolyte layer 23 are disposed opposite to each other. Then, the separator 24 is disposed between the positive electrode 21 and the negative electrode 22 so as to be pressed. Thus, an electrode laminate is formed. Then, the electrode laminate is wound in the lengthwise direction so that the wound electrode 25 is formed.

Finally, the wound electrode 25 is sandwiched by the casing film 26 constituted by an insulating material. Then, the resin film 29 is disposed in each of portions in which the positive-electrode terminal 27 and the negative-electrode terminal 28 overlap the casing film 26. Then, the outer periphery of the casing film 26 is sealed to insert the positive-electrode terminal 27 and the negative-electrode terminal 28 into the sealing portion of the casing film 26. Moreover, the wound electrode 25 is hermetically enclosed in the casing film 26. Thus, the gel electrolyte battery 20 is manufactured.

The casing film 26 is constituted by sequentially laminating a first polyethylene terephthalate layer 26a, an aluminum layer 26b, a second polyethylene terephthalate layer 26c and a straight-chain and low-density polyethylene layer 26d in this order, as shown in Fig. 14. The straight-chain and low-density polyethylene layer 26d serves as a heat welding layer. When the wound electrode 25 is enclosed, the straight-chain and low-density polyethylene layer 26d is disposed on the inside. The heat welding layer may be constituted by a material, such as polyethylene terephthalate, nylon, cast

polypropylene or high-density polyethylene as well as straight-chain and low-density polyethylene.

Note that the structure of the casing film 26 is not limited to the foregoing structure. The necessity is such that at least one aluminum layer is present in the layer and the thermo-fusible polymer film is present on at least one surface.

When the wound electrode 25 is packed in the casing film 26, the resin film 29 is disposed in each of the portions in which the casing film 26 and the positive-electrode terminal 27 and the negative-electrode terminal 28 are brought into contact with each other. Thus, occurrence of short circuit caused from burrs of the casing film 26 can be prevented. Moreover, adhesiveness between the casing film 26 and the positive-electrode terminal 27 and between the casing film 26 and the negative-electrode terminal 28 can be improved.

The material of the resin film 29 must have adhesiveness with respect to the positive electrode terminal 17 and the negative electrode terminal 18. When the foregoing requirement is satisfied, the material is not limited. It is preferable that any one of the following materials is employed: polyethylene, polypropylene, denatured polyethylene, denatured polypropylene, their copolymers and polyolefine resin. It is preferable that the thickness of the resin film 29 satisfies a range from 20  $\mu\text{m}$  to 300  $\mu\text{m}$  realized before the heat welding operation is performed. When the thickness of the resin film 29 is larger than 20  $\mu\text{m}$ , handling easiness deteriorates. When the thickness is larger than 300  $\mu\text{m}$ , water penetration easily takes place. Thus, the

airtightness in the battery cannot easily be maintained.

In the foregoing embodiment, the elongated positive electrode 21 and the elongated negative electrode 22 are laminated. Then, the laminate is wound in the lengthwise direction so that the wound electrode 25 is formed. The present invention is not limited to the foregoing structure. A rectangular positive electrode 21 and a rectangular negative electrode 22 may be laminated to form a wound electrode. Another structure may be employed in which the electrode laminate is alternately folded.

In the foregoing embodiment, the electrolyte to be interposed between the positive electrode 21 and the negative electrode 22 is the gel electrolyte containing the matrix polymer, the electrolyte salt and the solvent. The present invention is not limited to the foregoing structure. The present invention may be applied to a structure in which a solid electrolyte which does not contain solvent is employed and a structure in which electrolytic solution which does not contain the matrix polymer is employed.

The shape of the gel electrolyte battery 20 according to this embodiment is not limited. For example, a cylindrical shape, a rectangular shape or a coin shape may be employed. Moreover, the size may be a variety of sizes including a thin structure and a large-size structure. The present invention may be applied to both of the primary battery and a secondary battery.

### Examples

To confirm the effects of the invention, batteries having the foregoing structures

were manufactured to evaluate their characteristics.

### First Experiment

In Examples 1 to 7 and Comparative Example 1, the separators according to the first embodiment were used to manufacture batteries so as to evaluate their characteristics.

### Manufacturing of Sample Batteries

#### Example 1

Initially, the positive electrode was manufactured.

Initially, marketed lithium carbonate and cobalt carbonate were mixed with each other in such a manner that the composition ratio of lithium atoms and cobalt atoms was 1:1. Then, the mixture was baked for five hours in air at 900°C. Thus, cobalt acid lithium serving as the positive-electrode active material was obtained. The mean particle size of cobalt acid lithium was 10  $\mu\text{m}$ .

Then, 91 parts by weight of the obtained positive-electrode active material, 6 parts by weight of graphite serving as a conductive material and 3 parts by weight of polyvinylidene fluoride serving as the binder were mixed with one another so that a positive-electrode mix was prepared. Then, the positive-electrode mix was dispersed in N-methyl-2-pyrrolidone so as to be formed into paste.

Then, the obtained positive-electrode mix paste was uniformly applied to the two sides of an elongated aluminum foil serving as the positive electrode collector and having a thickness of 20  $\mu\text{m}$ . Then, the aluminum foil was subjected to a drying

process. After the drying process was completed, a roller press was operated to compress and mold the aluminum foil. Thus, a positive-electrode active material layer having a thickness of 40  $\mu\text{m}$  was formed. Then, a lead wire constituted by aluminum was welded to a portion of the positive electrode collector in which the positive-electrode active material layer was not formed. Thus, a positive electrode terminal was formed. As a result, the positive electrode was manufactured. The density of the positive-electrode active material layer was 3.6  $\text{g/cm}^3$ .

Then, the negative electrode was manufactured as follows.

Initially, methocarbon microbeads having a mean particle size of 25  $\mu\text{m}$  was baked at 2800°C so that graphite serving as the negative-electrode active material was obtained.

Then, 90 parts by weight of the obtained negative-electrode active material and 10 parts by weight of polyvinylidene fluoride were mixed so that a negative-electrode mix was prepared. Then, the negative-electrode mix was dispersed in N-methyl-2-pyrrolidone serving as the solvent so as to be formed into paste.

Then, obtained negative-electrode mix paste was uniformly applied to the two sides of elongated copper foil serving as the negative electrode collector and having a thickness of 15  $\mu\text{m}$ . Then, a drying process was performed. After the elongated copper foil has been dried, a roller press was operated to perform a compression molding operation. Thus, a negative-electrode active material layer having a thickness of 55  $\mu\text{m}$  was formed. Then, a nickel lead wire was welded to a portion of the negative

electrode collector in which the negative-electrode active material layer was not formed so that a positive electrode terminal was formed. The density of the negative-electrode active material layer was  $1.6 \text{ g/cm}^3$  at this time.

Then, a gel electrolyte layer was formed on each of the positive electrode and the negative electrode.

Initially, 80 g of dimethyl carbonate, 40 g of ethylene carbonate, 40 g of polypropylene carbonate, 9.2 g of  $\text{LiPF}_6$ , 0.8 g of vinylene carbonate and 0.8 g of 2, 4-difluoroanisole were mixed with each other so that solution was prepared. Then, the solution was added with 10 g of a copolymer (copolymerization weight ratio  $\text{PVdF:HFP} = 97:3$ ) of polyvinylidene fluoride (PVdF) and hexafluoropolypropylene (HFP). Then, a homonizer was operated to perform uniform dispersion. Then, heating and stirring were performed at  $75^\circ\text{C}$  until a colorless and transparent state was realized. Thus, electrolyte solution was prepared.

Then, the obtained electrolyte solution was uniformly applied to the two sides of each of the positive electrode and the negative electrode by the doctor blade method. Then, the positive electrode and the negative electrode applied with the electrolyte solution were allowed to stand in a drying unit, the inside portion of which was maintained at  $40^\circ\text{C}$ , for one minute. Thus, the electrolyte solution was gelled so that a gel electrolyte layer having a thickness of about  $8 \mu\text{m}$  was formed on each of the two sides of each of the positive electrode and the negative electrode.

Then, the battery was assembled as follows.



Initially, the thus-manufactured elongated positive electrode incorporating the gel electrolyte layer formed on each of the two sides thereof and the elongated negative electrode incorporating the gel electrolyte layer formed on each of the two sides thereof were laminated through a separator so that a laminate was obtained. Then, the laminate was wound in its lengthwise direction so that a wound electrode was obtained. The separator was a porous polyethylene film having a vacancy ratio of 36 % and a thickness of 8  $\mu\text{m}$ .

The wound electrode was sandwiched by a moisture-proof casing film formed by laminating a nylon sheet having a thickness of 25  $\mu\text{m}$ , an aluminum sheet having a thickness of 40  $\mu\text{m}$  and a polypropylene sheet having a thickness of 30  $\mu\text{m}$ . Then, the outer periphery of the casing film was welded with heat under reduced polyethylene so as to be sealed. Thus, the wound electrode was hermetically enclosed in the casing film. At this time, the positive electrode terminal and the negative electrode terminal were sandwiched in the sealing portions of the casing film. Moreover, a polyolefine film was disposed in each of the portions in which the casing film and the positive electrode terminal and the negative electrode terminal are in contact with each other.

Finally, the electrode elements were subjected to heat treatment in a state where the electrode terminals were enclosed in the casing film. Thus, the gel electrolyte battery was manufactured.

#### Example 2

A process similar to that according to Example 1 was performed except for the separator which was, in this example, a porous polyethylene film having a vacancy ratio of 37 % and a thickness of 9  $\mu\text{m}$ . Thus, a gel electrolyte battery was manufactured.

#### Example 3

A process similar to that according to Example 1 was performed except for the separator which was, in this example, a porous polyethylene film having a vacancy ratio of 35 % and a thickness of 10  $\mu\text{m}$ . Thus, a gel electrolyte battery was manufactured.

#### Example 4

A process similar to that according to Example 1 was performed except for the separator which was, in this example, a porous polyethylene film having a vacancy ratio of 30 % and a thickness of 12  $\mu\text{m}$ . Thus, a gel electrolyte battery was manufactured.

#### Example 5

A process similar to that according to Example 1 was performed except for the separator which was, in this example, a porous polyethylene film having a vacancy ratio of 39 % and a thickness of 15  $\mu\text{m}$ . Thus, a gel electrolyte battery was manufactured.

#### Example 6

A process similar to that according to Example 1 was performed except for the

separator which was, in this example, a porous polyethylene film having a vacancy ratio of 36 % and a thickness of 8  $\mu\text{m}$ . Thus, a gel electrolyte battery was manufactured.

#### Example 7

A process similar to that according to Example 1 was performed except for the separator which was, in this example, a porous polyethylene film having a vacancy ratio of 36 % and a thickness of 16  $\mu\text{m}$ . Thus, a gel electrolyte battery was manufactured.

#### Comparative Example 1

A process similar to that according to Example 1 was performed except for omission of the separator in this comparative example. Thus, a gel electrolyte battery was manufactured.

#### Evaluation of Characteristics of Sample Batteries

The materials, vacancy ratios, thicknesses, breaking strength and breaking ductility of the separators according to Examples 1 to 7 were collectively shown in Table 1.

Table 1

	Material	Vacancy Ratio (%)	Thickness ( $\mu\text{m}$ )	Breaking Strength ( $\text{kg}/\text{cm}^2$ )	Breaking Ductility (%)
Example 1	polyethylene	36	8	739	161

Example 2	polyethylene	37	9	1185	156
Example 3	polyethylene	35	10	1300	164
Example 4	polyethylene	30	12	1409	170
Example 5	polyethylene	39	15	1179	137
Example 6	polypropylene	36	8	1650	139
Example 7	polypropylene	36	16	1946	127

### Evaluation of Charge and Discharge Characteristics

The thus-manufactured batteries were subjected to charge and discharge tests so that the characteristics of the batteries were evaluated. A potentio-galvanostat was operated to perform the charge and discharge tests of the batteries. A constant-current and constant-voltage method was employed to perform the charge and discharge.

Initially, each battery was charged with a constant current of 200 mA. When the voltage of the closed circuit was raised to 4.2 V, the constant-current charge was changed to the constant-voltage charge. Then, the constant-voltage charge was continued. The charge was completed nine hours after start of the charging operation. Then, discharge was performed with a constant current of 200 mA. When the voltage of the closed circuit was raised to 3.0 V, the discharge was completed.

The charge and discharge capacities of each battery were detected. Moreover, a charge and discharge efficiency and an energy density of each battery were calculated.

The detected charge capacity, the discharge capacity, the charge and discharge

efficiency and the energy density of each of the batteries according to Examples 1 to 7 and Comparative Example 1 were shown in Table 2.

Table 2

	Initial Charge Capacity (mAh/g)	Initial Discharge Capacity (mAh/g)	Charge and Discharge Efficiency (%)	Energy Density (Wh/l)
Example 1	710	611	86	332
Example 2	709	608	86	331
Example 3	711	606	85	330
Example 4	708	609	86	331
Example 5	710	606	85	330
Example 6	497	352	71	189
Example 7	512	355	69	191
Comparative Example 1	1503	349	23	187

As can be understood from Table 2, the batteries according to Examples 1 to 7 were excellent in all of the charge capacity, the discharge capacity, the charge and discharge efficiency and the energy density. Thus, the designed excellent characteristics were realized. In particular, the batteries each incorporating the polyethylene separator and according to Examples 1 to 5 were excellent in the characteristics.

On the other hand, the battery according to Comparative Example 1 encountered small short circuit during the charging operation. That is, satisfactory battery characteristics were not obtained.

#### Evaluation of Safety of Sample Batteries

The shutdown start temperature of the separator of each of the batteries according to Examples 1 to 7 and Comparative Example 1 and the highest surface temperature of each battery when the battery was externally short-circuited were examined.

The shutdown temperature was measured such that the battery was heated at a rising ratio of 5°C/minute. When the AC resistance was raised by two or more digits owing to application of 1 kHz, the temperature of each battery was measured.

The temperature of the surface of the battery realized when the battery was externally short-circuited was measured such that the battery was charged under similar conditions to those for the charge and discharge tests. Then, the battery was heated to 60°C. In the foregoing state, the highest temperature of the battery realized when the terminals were short-circuited by using a 12 mΩ resistor was measured by using a thermo-couple.

The shutdown temperature and the temperature of the surface of each of the batteries according to Examples 1 to 7 and Comparative Example 1 realized when external short circuit was caused to occur were shown in Table 3.

Table 3

	Shutdown Start Temperature (°C)	Temperature of Surface of Battery when External Short Circuit was Caused to Occur (°C)
Example 1	126	118
Example 2	126	119
Example 3	125	117
Example 4	126	118
Example 5	123	116
Example 6	163	161
Example 7	165	165
Comparative Example 1	—	200 or higher

As can be understood from Table 3, each of the batteries according to Examples 1 to 5 and incorporating the separator constituted by polyethylene encountered shutdown in a temperature range from 100°C to 160°C. The relationship between the temperature of the battery according to Example 1 and the impedance in the battery was shown in Fig. 15. As can be understood from Fig. 15, the impedance in the battery was rapidly enlarged when the temperature of the battery was about 126°C.

The batteries according to Examples 6 and 7 and each incorporating the separator constituted by polypropylene encountered shutdown in spite of the temperature being 160°C or higher. The relationship between the temperature of the battery according to Example 6 and the impedance in the battery was shown in Fig. 16.

As can be understood from Fig. 16, the impedance in the battery was rapidly enlarged when the temperature of the battery was about 163°C.

The temperature of the surface of each of the batteries according to Examples 1 to 5 when the charged battery was externally short-circuited was 120°C or lower. Thus, heat generation occurring when the battery was erroneously operated was effectively prevented. Hence it follows that the safety of the battery was secured. On the other hand, the temperature of the surface of each of the batteries according to Examples 6 and 7 was raised to 160°C when the charged battery was externally short-circuited. Thus, great heat generation occurs when the battery was used erroneously. The batteries according to Examples 1 to 7 encountered the shutdown effect were free from any smoke from the inside portion of the battery when the charged battery was externally short-circuited.

On the other hand, the battery according to Comparative Example 1 was free from any shutdown effect when the temperature of the battery was raised to 180°C. When the charged battery was externally short-circuited, the temperature of the surface of the battery was raised to 200°C. Moreover, smoke from the inside portion of the battery occurred.

#### Specification of Physical Properties of Separator

The relationship between the breaking strength and the breaking ductility of the separator of each of the batteries according to Examples 1 to 7 was shown in Fig. 17. As can be understood from Fig. 17 and results of the evaluation of the characteristics



of the battery, the breaking strength of the separator of each of the batteries according to Examples 1 to 5 and from which excellent characteristics of the battery were obtained was lower than  $1650 \text{ kg/cm}^2$ . Moreover, the breaking ductility was 135 % or higher. The foregoing mechanical strength was realized.

A fact was confirmed that all of the separators each having the foregoing mechanical strength had the fibril structure shown in Fig. 6. An electronic microscope photograph of the fine structure of the separator according to Example 6 at a magnification of 50,000 times was shown in Fig. 18. When a comparison between Figs. 6 and 18 was made, a fact was understood that the mechanical strength of the separator concerns its fine structure. To realize the foregoing mechanical strength, the fine structure of the separator must be the fibril structure.

As a result, use of the porous polyolefine separator having the thickness satisfying a range not smaller than  $5 \mu\text{m}$  nor larger than  $15 \mu\text{m}$ , the vacancy ratio satisfying the range not lower than 25 % nor higher than 60 % and the shutdown effect when the temperature of the battery satisfied the range from  $100^\circ\text{C}$  or higher to  $160^\circ\text{C}$  or lower enabled both of a high energy density and safety of the battery to be realized.

Another fact was understood that use of the porous polyolefine film having the thickness satisfying the range not smaller than  $5 \mu\text{m}$  nor larger than  $15 \mu\text{m}$ , the vacancy ratio satisfying the range not lower than 25 % nor higher than 60 %, the breaking strength lower than  $1650 \text{ kg/cm}^2$  and the breaking ductility not lower than 135 % enabled both of a high energy density and safety of the battery to be realized.

## Second Experiment

In each of the following Examples 8 and 9 and Comparative Example 2, the separator according to the second embodiment was employed to manufacture batteries to evaluate their characteristics.

### Example 8

The positive electrode was manufactured such that 95 wt% of  $\text{LiCoO}_2$  serving as the positive-electrode active material, 2 wt% of graphite serving as a conductive material and 3 wt% of polyvinylidene fluoride were mixed with one another. Thus, a positive-electrode mix was prepared. Then, N-methyl pyrrolidone was added in a quantity which was 0.6 time the quantity of the positive-electrode mix so that slurry was prepared.

Then, obtained slurry was uniformly applied to either side of the aluminum foil which was formed into the positive electrode collector by the doctor blade method. Then, the aluminum foil was dried at high temperatures to remove N-methyl pyrrolidone. Thus, a positive-electrode active material layer was formed. Finally, a roll press was operated to apply proper polyethylene to perform a pressing operation. Thus, the sample was cut to have a size 300 mm  $\times$  50 mm so that the positive electrode was manufactured. A columnar aluminum piece was spot-welded to the positive electrode so that a positive electrode terminal was formed.

To manufacture the negative electrode, 91 wt% of graphite serving as the negative-electrode active material and 9 wt% of polyvinylidene fluoride serving as the

binder were mixed with each other so that the negative-electrode mix was prepared. Then, N-methyl pyrrolidone was added in a quantity which was 1.1 time the quantity of the negative-electrode mix so that slurry was prepared.

Then, obtained slurry was uniformly applied to either side of the copper foil which was formed into the negative electrode collector by the doctor blade method. Then, the copper foil was dried to remove N-methyl pyrrolidone so that the negative-electrode active material layer was formed. Finally, the roll press was operated to apply proper polyethylene to perform a pressing operation. Thus, the sample was cut to have a size 370 mm  $\times$  52 mm so that the negative electrode was manufactured. Then, a copper rod was spot-welded to the negative electrode so that the negative electrode terminal was formed.

On the other hand, 6.7 wt% of polyvinylidene fluoride, 9.2 wt% of ethylene carbonate, 11.6 wt% of polypropylene carbonate, 2.3 wt% of  $\gamma$ -butyrolactone, 6.67 wt% of dimethyl carbonate and 3.5 wt% of  $\text{LiPF}_6$  were mixed with one another. Thus, polymer electrolyte solution was prepared. Note that dimethyl carbonate served as solvent for dissolving polyvinylidene fluoride.

The obtained polymer electrolyte solution in the state of liquid was applied to the surface of each of the positive electrode and the negative electrode by the doctor blade method. Then, the positive electrode and the negative electrode were dried for three minutes in a constant-temperature tank set to 35°C. Thus, a thin film was formed. At this time, dimethyl carbonate was not left in the polymer electrolyte. The

application operation was performed in such a manner that the thickness of the polymer electrolyte on each of the positive electrode and the negative electrode was 10  $\mu\text{m}$ .

The separator was a separator constituted by a composite material of polyethylene and polypropylene and having a thickness of 10  $\mu\text{m}$ . The ratio of polyethylene and polypropylene in the composite material was 1:1. The separator constituted by the composite material was manufactured as follows.

Initially, 100 parts by weight of a polyolefine mixture composed of 20 wt% of ultra high molecular weight polyethylene (UHMWPE) having a weight average molecular weight  $M_w$  of  $2.5 \times 10^6$ , 30 wt% of high-density polyethylene (HDPE) having a weight average molecular weight  $M_w$  of  $3.5 \times 10^5$  and 50 wt% of polypropylene having a weight average molecular weight  $M_w$  of  $5.1 \times 10^5$  was added with 0.375 part by weight of oxidation inhibitor so that a polyolefine composition was prepared.

Then, 30 parts by weight of the polyolefine composition were introduced into a biaxial extruder (having a diameter of 58 mm,  $L/D = 42$  and a strong kneading type). Moreover, 70 parts by weight of liquid paraffin were supplied through a side feeder of the biaxial extruder so as to be melted and kneaded at 200 rpm. Thus, polyolefine solution was prepared in the extruder.

Then, the polyolefine solution was extruded from a T-die disposed at the leading end of the extruder at 190°C so as to be wound around a cooling roll. Thus,

a gel sheet was molded. Then, the gel sheet was simultaneous double-axis oriented at 115°C to obtain a 5 × 5 oriented film. The obtained oriented film was cleaned with methylene chloride to extract and remove liquid paraffin. Then, the oriented film was dried and subjected to heat treatment. Thus, a fine-porous separator constituted by a composite material of polyethylene and polypropylene was obtained.

The thus-manufactured elongated positive electrode having the gel electrolyte layer and the elongated negative electrode having the gel electrolyte layer were laminated through the separator so that a laminate was formed. Then, the laminate was wound in its lengthwise direction. Thus, a 36 mm × 52 mm × 5 mm wound electrode was obtained.

Then, the wound electrode was sandwiched by a casing film constituted by a moisture-proof multilayered film having a thickness of 100 μm. Then, the outer periphery of the casing film was heat-welded under reduced pressure so as to be sealed. Thus, the wound electrode was hermetically sealed in the casing film. At this time, the positive electrode terminal and the negative electrode terminal were sandwiched in the sealing portions of the casing film.

#### Example 9

A process similar to that according to Example 8 was performed except for a separator which was, in this example, obtained by bonding a polyethylene separator having a thickness of 5 μm and a polypropylene separator having a thickness of 5 μm to each other. Thus, a battery was manufactured.

### Comparative Example 2

A process similar to that according to Example 8 was performed except for a separator which was, in this example, a polyethylene separator having a thickness of 10  $\mu\text{m}$ . Thus, a battery was manufactured.

Each of the thus-manufactured batteries were charged and discharged several times. In a discharged state, the battery was introduced into a constant-temperature tank. While measuring the resistance with 1 kHz, the temperature was raised to 140°C, 145°C, 150°C, 155°C, 160°C, 165°C and 170°C at a rising rate of 5°C/minute. Then, each temperature was maintained for 30 minutes. When the resistance was not decreased in the period in which the predetermined temperature was maintained, a determination was made that no short circuit occurred. When the resistance was decreased, a determination was made that short circuit occurred.

Results were shown in Table 4.

Table 4

	Example 8	Example 9	Comparative Example 2
140°C	○	○	○
145°C	○	○	○
150°C	○	○	×
155°C	○	○	×
160°C	○	○	×

165°C	○	○	×
170°C	×	×	×

The batteries according to Examples 8 and 9 incorporated the separator constituted by the composite material of polyethylene and polypropylene and the separator constituted by bonding the polyethylene separator and the polypropylene separator to each other. As compared with the battery according to Comparative Example 2 and incorporating the separator constituted by only polyethylene, the melt-down temperature was raised by about 15°C. The battery incorporating the separator having the high melt-down temperature enabled the temperature at which the internal short circuit started owing to the meltdown to be raised. Therefore, when the temperature of the battery was raised, occurrence of the internal short circuit can be prevented as compared with the polyethylene separator. Thus, prevention of heat generation from the battery caused from the internal short circuit was permitted.

The manufactured battery was charged and discharged several times. Then, the battery in an overcharged state of 4.4 V was introduced into a high-temperature tank. While measuring the resistance with 1 kHz, the temperature was raised to 135°C, 140°C, 145°C, 150°C and 155°C at a rising ratio of 5°C/minute. Each temperature was maintained for 30 minutes. When the resistance was not decreased during retention at the predetermined temperature, a determination was made that no short circuit occurred. When the resistance was decreased, a determination was made that

short circuit occurred. Since the voltage was 4.4 V or higher in the foregoing case, heat was sometimes generated owing to short circuit. Therefore, the measurement was completed when a fact that the resistance was decreased was confirmed.

Results were shown in Table 5.

Table 5

	Example 8	Example 9	Comparative Example 2
135°C	○	○	○
140°C	○	○	×
145°C	○	○	×
150°C	×	○	×
155°C	×	×	×

Even in an abnormal state of overcharge at 4.4 V, the batteries according to Example 8 and Example 9 which incorporated the separator constituted by the composite material of polyethylene and polypropylene and the separator constituted by bonding the polyethylene separator and the polypropylene separator to each other enabled the melt-down temperature to be raised by about 15°C as compared with the battery according to Comparative Example 2. The battery according to Comparative Example 2 incorporated the separator constituted by only polyethylene. The battery incorporated the separator having the high melt-down temperature enabled the



temperature at which the internal short circuit started owing to meltdown to be raised. When the temperature of the battery was raised, short circuit did not easily occur as compared with the polyethylene separator. Thus, heat generation of the battery owing to the internal short circuit can be prevented.

In the present invention, the separator constituted by the porous polyolefine film, the separator constituted by the composite material of polyethylene and polypropylene or the separator formed by bonding the first separator constituted by polyethylene and the second separator constituted by the polypropylene, the mechanical characteristics and thermal characteristics of which are specified are employed. Therefore, both of raising of the energy density and improvement in the safety can be realized as distinct from the conventional technique. Thus, the high-performance solid electrolyte battery excellent in the characteristics as the battery and safety can be realized.

Although the invention has been described in its preferred form and structure with a certain degree of particularity, it is understood that the present disclosure of the preferred form can be changed in the details of construction and in the combination and arrangement of parts without departing from the spirit and the scope of the invention as hereinafter claimed.

WHAT IS CLAIMED IS:

1. A solid electrolyte battery comprising:  
a positive electrode;  
a negative electrode disposed opposite to said positive electrode;  
a separator disposed between said positive electrode and said negative electrode; and

solid electrolytes each of which is disposed between said positive electrode and said separator and between said separator and said negative electrode, wherein

said separator is constituted by a polyolefine porous film, said polyolefine porous film has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$  and a vacancy ratio satisfying a range not lower than 25 % nor higher than 60 %, and the impedance in said solid electrolyte battery is higher than the impedance realized at the room temperature when the temperature of said solid electrolyte battery satisfies a range not lower than 100°C nor higher than 160°C.

2. A solid electrolyte battery according to claim 1, wherein said porous polyolefine film contains polyethylene.

3. A solid electrolyte battery according to claim 1, wherein said solid electrolyte is a gel electrolyte containing swelling solvent.

4. A solid electrolyte battery according to claim 1, wherein said electrodes consist of a positive electrode using lithium ions as electrode reaction species and a negative electrode constituted by a carbonaceous material.

5. A solid electrolyte battery according to claim 3, wherein said solid electrolyte is a gel electrolyte containing ethylene carbonate, polypropylene carbonate and  $\text{LiPF}_6$ .

6. A solid electrolyte battery according to claim 5, wherein said solid electrolyte is a gel electrolyte further containing vinylene carbonate and/or 2, 4-difluoroanisole.

7. A solid electrolyte battery according to claim 6, wherein the content of each of vinylene carbonate and 2, 4-difluoroanisole is not higher than 5 wt% of the overall weight of said solid electrolyte.

8. A solid electrolyte battery according to claim 7, wherein a gel electrolyte is employed which is constituted by polyvinylidene fluoride or a copolymer of polyvinylidene fluoride.

9. A solid electrolyte battery according to claim 8, wherein a copolymer is

used which contains polyvinylidene fluoride and polyhexafluoropolypropylene.

10. A solid electrolyte battery according to claim 9, wherein said gel electrolyte is composed of a copolymer constituted by polyvinylidene fluoride and polyhexafluoropolypropylene such that polyhexafluoropolypropylene is contained in a quantity smaller than 8 wt%.

11. A solid electrolyte battery comprising:  
a positive electrode;  
a negative electrode disposed opposite to said positive electrode;  
a separator disposed between said positive electrode and said negative electrode; and

solid electrolytes each of which is disposed between said positive electrode and said separator and between said separator and said negative electrode, wherein

said separator is constituted by a polyolefine porous film, said polyolefine porous film has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$ , a vacancy ratio satisfying a range not lower than 25 % nor higher than 60 %, breaking strength lower than 1650  $\text{kg/cm}^2$  and breaking ductility not lower than 135 %.

12. A solid electrolyte battery according to claim 11, wherein said porous

polyolefine film contains polyethylene.

13. A solid electrolyte battery according to claim 11, wherein said solid electrolyte is a gel electrolyte containing swelling solvent.

14. A solid electrolyte battery according to claim 11, wherein said electrodes consist of a positive electrode using lithium ions as electrode reaction species and a negative electrode constituted by a carboneous material.

15. A solid electrolyte battery according to claim 13, wherein said solid electrolyte is a gel electrolyte containing ethylene carbonate, polypropylene carbonate and  $\text{LiPF}_6$ .

16. A solid electrolyte battery according to claim 15, wherein said solid electrolyte is a gel electrolyte further containing vinylene carbonate and/or 2, 4-difluoroanisol.

17. A solid electrolyte battery according to claim 15, wherein the content of each of vinylene carbonate and 2, 4-difluoroanisol is not higher than 5 wt% of the overall weight of said solid electrolyte.

18. A solid electrolyte battery according to claim 17, wherein a gel electrolyte is employed which is constituted by polyvinylidene fluoride or a copolymer of polyvinylidene fluoride.

19. A solid electrolyte battery according to claim 18, wherein a copolymer is used which contains polyvinylidene fluoride and polyhexafluoropolypropylene.

20. A solid electrolyte battery according to claim 19, wherein said gel electrolyte is composed of a copolymer constituted by polyvinylidene fluoride and polyhexafluoropolypropylene such that polyhexafluoropolypropylene is contained in a quantity smaller than 8 wt%.

~~21.~~ A solid electrolyte battery comprising:  
a positive electrode;  
a negative electrode disposed opposite to said positive electrode; a separator disposed between said positive electrode and said negative electrode; and  
solid electrolytes each of which is disposed between said positive electrode and said separator and between said separator and said negative electrode, wherein  
said separator is constituted by a composite material of polyethylene and polypropylene, said polyolefine porous film has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$ , the shutdown temperature is substantially the

same as the shutdown temperature of a separator constituted by polyethylene and the meltdown temperature is higher than the meltdown temperature of a separator constituted by polypropylene by a range satisfying a range not lower than 10°C nor higher than 30°C.

22. A solid electrolyte battery according to claim 21, wherein said solid electrolyte is a gel electrolyte containing swelling solvent.

23. A solid electrolyte battery according to claim 21, wherein said electrodes consist of a positive electrode using lithium ions as electrode reaction species and a negative electrode constituted by a carbonaceous material.

24. A solid electrolyte battery according to claim 22, wherein said solid electrolyte is a gel electrolyte containing ethylene carbonate, polypropylene carbonate and  $\text{LiPF}_6$ .

25. A solid electrolyte battery according to claim 24, wherein said solid electrolyte is a gel electrolyte further containing vinylene carbonate and/or 2, 4-difluoroanisole.

26. A solid electrolyte battery according to claim 25, wherein the content of

each of vinylene carbonate and 2, 4-difluoroanisol is not higher than 5 wt% of the overall weight of said solid electrolyte.

27. A solid electrolyte battery according to claim 26, wherein a gel electrolyte is employed which is constituted by polyvinylidene fluoride or a copolymer of polyvinylidene fluoride.

28. A solid electrolyte battery according to claim 27, wherein a copolymer is used which contains polyvinylidene fluoride and polyhexafluoropolypropylene.

29. A solid electrolyte battery according to claim 28, wherein said gel electrolyte is composed of a copolymer constituted by polyvinylidene fluoride and polyhexafluoropolypropylene such that polyhexafluoropolypropylene is contained in a quantity smaller than 8 wt%.

~~30.~~ A solid electrolyte battery comprising:  
a positive electrode;  
a negative electrode disposed opposite to said positive electrode;  
a separator disposed between said positive electrode and said negative electrode; and  
solid electrolytes each of which is disposed between said positive electrode and



said separator and between said separator and said negative electrode, wherein

said separator is formed by bonding a first separator constituted by polyethylene and a second separator constituted by polypropylene to each other, said separator has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$  and said separator has a shutdown temperature which is substantially the same as the shutdown temperature of a separator constituted by polyethylene and a meltdown temperature which is substantially the same as the meltdown temperature of a separator constituted by polypropylene.

31. A solid electrolyte battery according to claim 30, wherein said solid electrolyte is a gel electrolyte containing swelling solvent.

32. A solid electrolyte battery according to claim 30, wherein said electrodes consist of a positive electrode using lithium ions as electrode reaction species and a negative electrode constituted by a carbonaceous material.

33. A solid electrolyte battery according to claim 31, wherein said solid electrolyte is a gel electrolyte containing ethylene carbonate, polypropylene carbonate and  $\text{LiPF}_6$ .

34. A solid electrolyte battery according to claim 33, wherein said solid

electrolyte is a gel electrolyte further containing vinylene carbonate and/or 2, 4-difluoroanisol.

35. A solid electrolyte battery according to claim 34, wherein the content of each of vinylene carbonate and 2, 4-difluoroanisol is not higher than 5 wt% of the overall weight of said solid electrolyte.

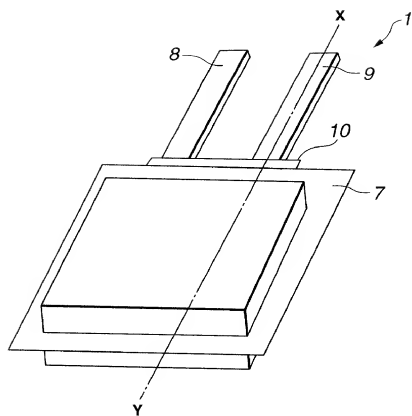
36. A solid electrolyte battery according to claim 35, wherein a gel electrolyte is employed which is constituted by polyvinylidene fluoride or a copolymer of polyvinylidene fluoride.

37. A solid electrolyte battery according to claim 36, wherein a copolymer is used which contains polyvinylidene fluoride and polyhexafluoropolypropylene.

38. A solid electrolyte battery according to claim 37, wherein said gel electrolyte is composed of a copolymer constituted by polyvinylidene fluoride and polyhexafluoropolypropylene such that polyhexafluoropolypropylene is contained in a quantity smaller than 8 wt%.

## ABSTRACT OF THE DISCLOSURE

A solid electrolyte battery having improved energy density and safety, the solid electrolyte battery incorporating a positive electrode; a negative electrode disposed opposite to the positive electrode; a separator disposed between the positive electrode and the negative electrode; and solid electrolytes each of which is disposed between the positive electrode and the separator and between the separator and the negative electrode, wherein the separator is constituted by a polyolefine porous film, the polyolefine porous film has a thickness satisfying a range not smaller than 5  $\mu\text{m}$  nor larger than 15  $\mu\text{m}$  and a vacancy ratio satisfying a range not lower than 25 % nor higher than 60 %, and the impedance in the solid electrolyte battery is higher than the impedance realized at the room temperature when the temperature of the solid electrolyte battery satisfies a range not lower than 100°C nor higher than 160°C.

**FIG.1**

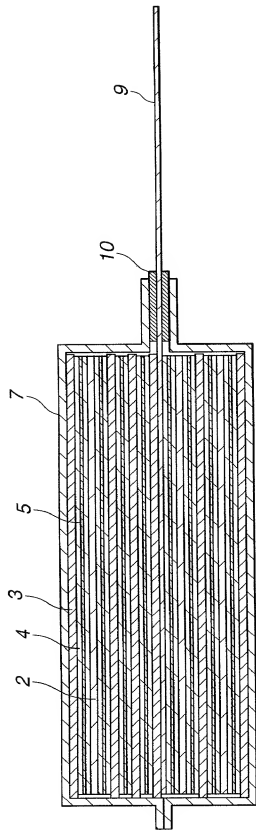
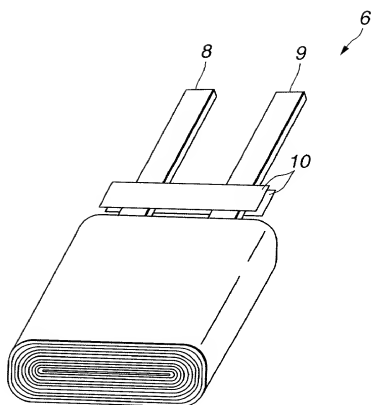
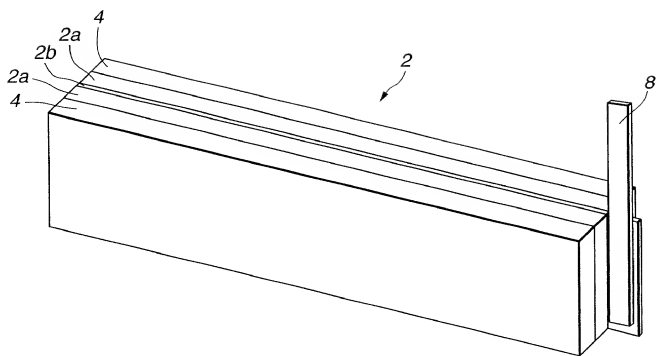


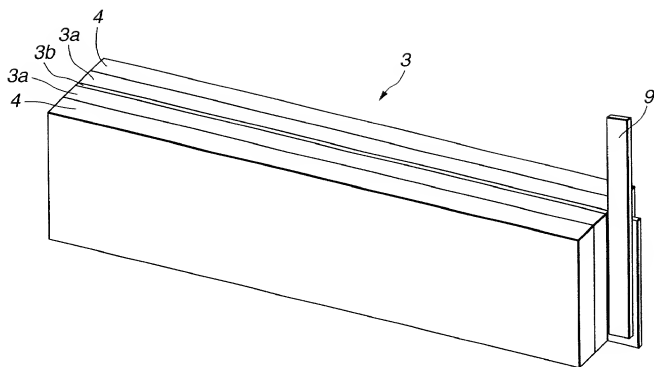
FIG.2



**FIG.3**



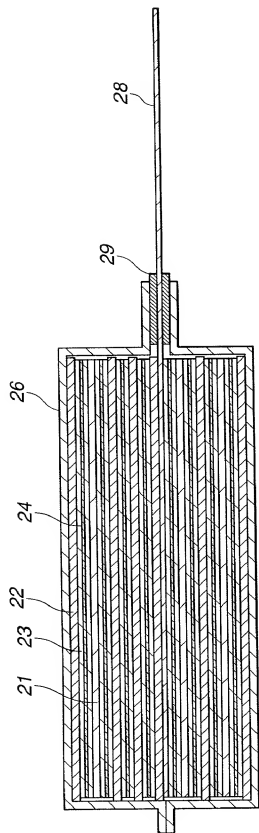
**FIG.4**



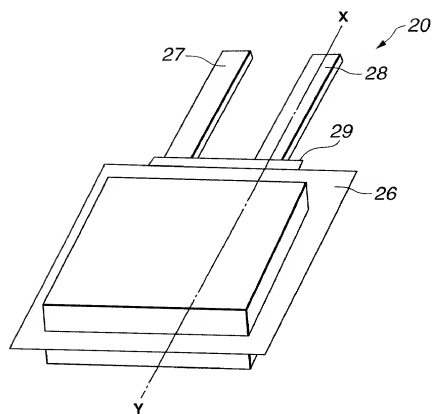
**FIG.5**



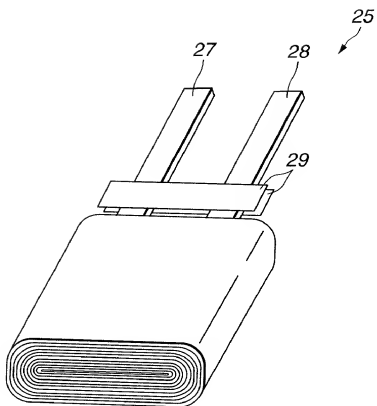
**FIG.6**



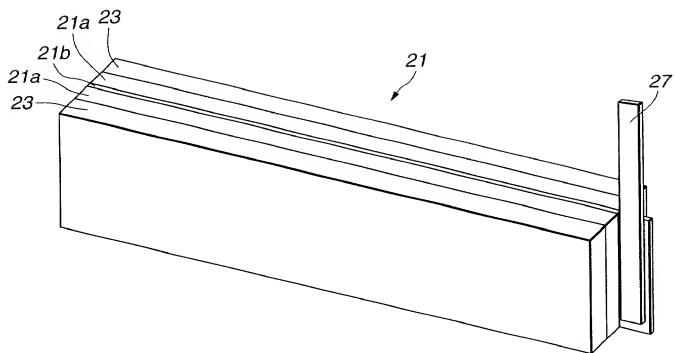
**FIG. 7**



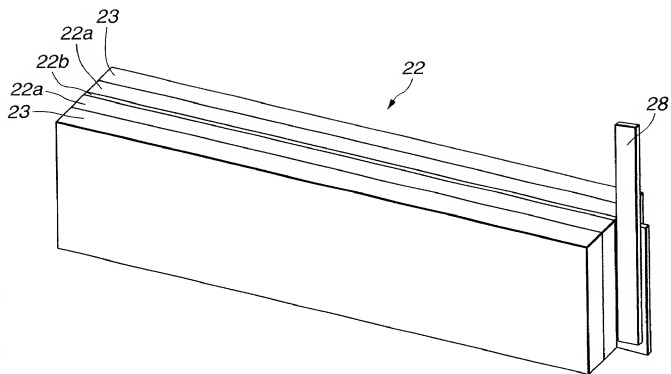
**FIG.8**



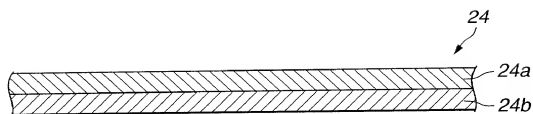
**FIG.9**



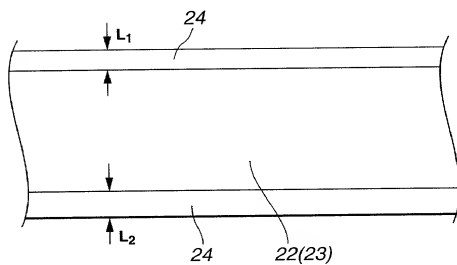
**FIG.10**



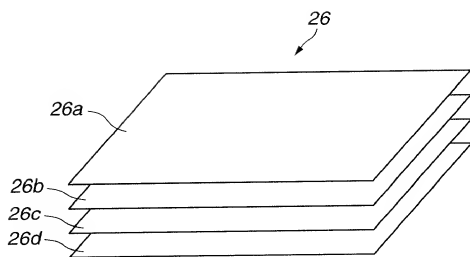
**FIG.11**



**FIG.12**



**FIG.13**



**FIG.14**



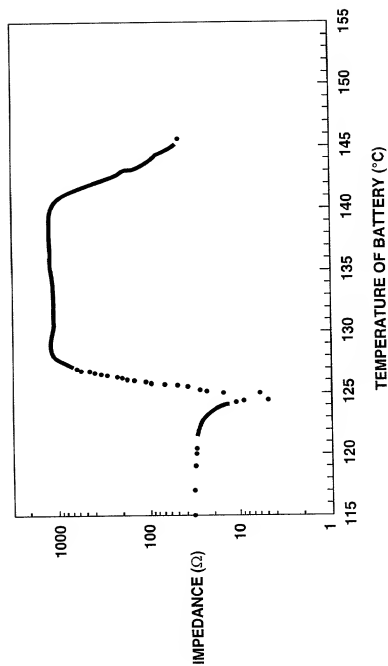
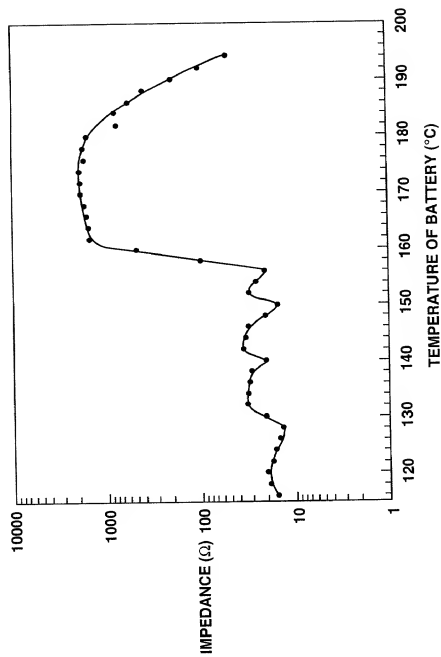
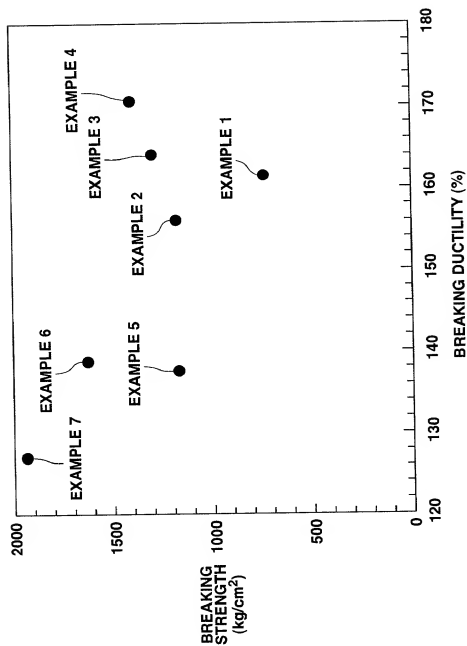


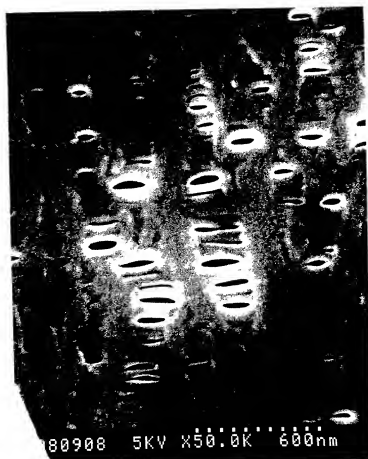
FIG.15



**FIG.16**



**FIG.17**



**FIG.18**

## DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

## SOLID ELECTROLYTE BATTERY

Case No. P00,0483, the specification of which

(check one) X is attached hereto.  
       was filed on \_\_\_\_\_, as  
 Application Serial No. \_\_\_\_\_  
 and was amended on \_\_\_\_\_  
 (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent Office all information which is known to me to be material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, 1.56.<sup>1</sup>

I do not know and do not believe this invention was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, and I believe that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as identified below:

I hereby claim foreign priority benefits under Title 35, United States Code, 119 of any foreign application(s) for patent or inventor's certificate listed below

Prior Foreign Application(s)

Number Country

Date

P11-146653

Japan

May 26, 1999

P11-365064

Japan

December 22, 1999

and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the above listed application on which priority is claimed:

Prior Foreign Application(s)

Number Country

Date

<sup>1</sup> (b) Under this section, information is material to patentability when it is not cumulative to information already of record or being made of record in the application, and

(1) It establishes, by itself or in combination with other information, a *prima facie* case of unpatentability of a claim; or  
 (2) It refutes, or is inconsistent with, a position the applicant takes in:

(i) Opposing an argument of unpatentability relied on by the Office, or  
 (ii) Asserting an argument of patentability.

A *prima facie* case of unpatentability is established when the information compels a conclusion that a claim is unpatentable under the preponderance of evidence, burden-of-proof standard, giving each term in the claim its broadest reasonable construction consistent with the specification, and before any consideration is given to evidence which may be submitted in an attempt to establish a contrary conclusion of patentability.

If no priority is claimed, I have identified all foreign patent applications filed prior to this application:  
 Prior Foreign Application(s)  
 Number Country Date

And I hereby appoint Messrs. John D. Simpson (Registration No. 19,842), Dennis A. Gross (24,410), Robert M. Barrett, (30,142), Steven H. Noll (28,982), Kevin W. Guynn (29,927), Robert M. Ward (26,517), Brett A. Valiquet (27,841), Edward A. Lehman (22,312), David R. Metzger (32,919), Todd S. Parkhurst (26,494), James D. Hobart (24,149), Melvin A. Robinson (31,870), Joseph P. Reagen (35,332), Michael R. Hull (35,902), Michael S. Leonard (37,557), William E. Vaughan (39,056) and Lewis T. Steadman (17,074), all members of the firm of Hill & Simpson, A Professional Corporation

Telephone: 312/876-0200 Ext. 3491

my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and direct that all correspondence be forwarded to:

Hill & Simpson

A Professional Corporation

85th Floor Sears Tower, Chicago, Illinois 60606

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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